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**U.S. Army
Environmental
Center**

**FORT DEVENS
FEASIBILITY STUDY
FOR GROUP 1A SITES**

**FINAL
PLOW SHOP POND SUPPLEMENTAL INVESTIGATION
WORK PLAN
DATA ITEM A004**

CONTRACT DAAA15-91-D-0008

**U.S. ARMY ENVIRONMENTAL CENTER
ABERDEEN PROVING GROUND, MARYLAND**

SEPTEMBER 1994

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DELIVERY ORDER NUMBER 0004

Prepared for:

U.S. Army Environmental Center
Aberdeen Proving Ground, Maryland

Prepared by:

ABB Environmental Services, Inc.
Portland, ME
Project No. 07005-01

SEPTEMBER 1994

**PLOW SHOP POND SUPPLEMENTAL INVESTIGATION
WORK PLAN
FORT DEVENS, MASSACHUSETTS**

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1.0 INTRODUCTION

ABB Environmental Services, Inc. (ABB-ES), prepared this work plan as part of the Feasibility Study (FS) for Group 1A Sites at Fort Devens, Massachusetts in accordance with the U.S. Army Environmental Center (USAEC, formerly U.S. Army Toxic and Hazardous Materials Agency) Contract DAAA15-91-D-0008, Delivery Order 0004. The Group 1A sites were identified for investigation in the Fort Devens Master Environmental Plan (Biang, 1992), and are subject to a Federal Facility Agreement (FFA or Interagency Agreement [IAG]) between the U.S. Department of the Army and the U.S. Environmental Protection Agency (USEPA). Fort Devens was placed on the National Priorities List (NPL) effective December 21, 1989.

The Group 1A sites consist of the sanitary landfill incinerator, Area of Contamination (AOC) 4; sanitary landfill No. 1 or Shepley's Hill Landfill, AOC 5; the asbestos cell, AOC 18; and Cold Spring Brook Landfill, AOC 40. AOCs 4 and 18 are co-located at AOC 5, and these three AOCs have been identified as the Shepley's Hill Landfill Operable Unit. Cold Spring Brook Landfill is included in the Cold Spring Brook Landfill Operable Unit. During the remedial investigation (RI) of Shepley's Hill Landfill, environmental contamination was detected in Plow Shop Pond. The Plow Shop Pond Operable Unit was identified to facilitate the management of additional investigations and evaluations in Plow Shop Pond. Figure 1 shows the location of Plow Shop Pond at Fort Devens.

1.1 PURPOSE AND SCOPE

The purpose of this work plan is to provide a basis and plan for collecting and interpreting data on the bioavailability and toxicity of sediment contaminants in Plow Shop Pond to facilitate the decision of whether and to what extent contaminated sediments found there should be remediated. In addition, the proposed activities will help to differentiate between the contribution to risk of landfill- and non-landfill-related analytes in Plow Shop Pond.

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1.2 SITE DESCRIPTION

Plow Shop Pond is a shallow, 30-acre pond located outside the installation boundary at the northeast corner of the Main Post at Fort Devens. Water elevation in Plow Shop Pond is controlled at approximately 216 feet above sea level by a dam located at the northwest corner of the pond. The central portion of the pond is approximately eight feet deep. A maximum depth of about ten feet occurs in the northeast arm of the pond. The discharge from the dam forms Nonacoicus Brook, which flows about 1 mile northwest before its confluence with the Nashua River.

Plow Shop Pond is the furthest downstream of a chain of six ponds (Long Pond, Sandy Pond, Flanagan Pond, Balch Pond, Grove Pond, and Plow Shop Pond) in the Town of Ayer. It receives drainage from approximately 17.7 square miles in the Towns of Ayer, Groton, and Harvard. Based on comparison to the Nashua River at East Pepperell, the 7-day 10-year low flow in Nonacoicus Brook at the pond outlet is approximately 2.6 cubic feet per second. The eastern shore of Plow Shop Pond is formed by a railroad causeway constructed in the 1800s. A stone arch culvert under the causeway connects the pond with Grove Pond.

The waters of Plow Shop Pond are designated as Class B by the Commonwealth of Massachusetts. The pond is eutrophic, and was classified in the RI Report as a floating-leaved deep marsh (E&E, 1993). Seasonally, more than 80 percent of the surface area of the pond is covered with aquatic macrophytes, including sweet water lily (*Nymphaea odorata*) and water shield (*Brasenia schreberi*). Submerged macrophytes (primarily water marigold [*Megalodonta beckii*]), seasonally cover more than 75 percent of the submerged portions of the pond. The pond bottom consists primarily of highly organic sediments and peat ranging in depth from approximately 1 foot to over 7 feet.

There are no residences or cottages along the pond shore. The eastern shore is formed by a railroad causeway and the southern and western shores border the Shepley's Hill Landfill area of Fort Devens. The northern shore borders the MOLUMCO Industrial Park in Ayer. The pond is used by area residents for recreational fishing.

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1.3 SUMMARY OF PREVIOUS INVESTIGATIONS

Environmental investigations were conducted at Plow Shop Pond in 1991 as part of the RI and in 1992 as part of supplemental RI activities. RI investigations consisted of collecting surface water and shallow (0 to 6 inch depth) sediment samples at 13 locations along the pond shoreline. Surface water samples were analyzed for Target Compound List (TCL) organics, Target Analyte List (TAL) metals, and several general analytical parameters. The volatile organic compounds (VOCs) chloroform and methylene chloride were reported in several samples, and the pesticide endrin was reported at a low concentration in one sample. Methylene chloride was considered a laboratory contaminant, and the endrin was not considered significant in the RI Report. The presence of chloroform, considered an improbable surface water contaminant in the RI Report, could not be explained. The inorganics copper, silver, and zinc exceeded Ambient Water Quality Criteria (AWQC) for the protection of aquatic life throughout the pond (E&E, 1993).

RI sediment samples were analyzed for TCL organics, TAL metals, and total organic carbon (TOC). The RI Report concluded that pond sediments were contaminated with high concentrations of TAL metals and low concentrations of several polynuclear aromatic hydrocarbons (PAHs). The VOCs acetone, methylene chloride, and 2-butanone were reported in several samples, as were low concentrations of 2,2-bis(para-chlorophenyl)-1,1-dichloroethene (DDE) and heptachlor (E&E, 1993). The presence of acetone, methylene chloride, and heptachlor is attributed to laboratory contamination.

During the supplemental RI, sediment samples (0 to 1 foot depth) were collected at 28 locations and analyzed for Project Analyte List (PAL) pesticides, polychlorinated biphenyls (PCBs), and inorganics. The RI Addendum Report concluded that sediments were contaminated with arsenic, barium, copper, chromium, iron, lead, manganese, mercury, nickel, and zinc. The supplemental sampling confirmed the presence of 2,2-bis(para-chlorophenyl)-1,1-dichloroethane (DDD), DDE, and 2,2-bis(para-chlorophenyl)-1,1,1-trichloroethane (DDT) at low concentrations in pond sediments.

In addition to sediment sampling, supplemental RI activities included macroinvertebrate community and fish community sampling and assessment, and fish tissue sampling and analysis for PAL metals. The results of these additional

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studies are discussed in the ecological risk assessment summary of Subsection 1.4.2.

1.4 SUMMARY OF HUMAN HEALTH AND ECOLOGICAL RISK ASSESSMENTS

The following subsections summarize the results of human health and ecological risk assessments conducted for Plow Shop Pond.

1.4.1 Summary of Human Health Risk Assessment

A supplemental human health risk assessment was performed in the RI Addendum Report (ABB-ES, 1993b) to update the RI risk assessment completed in April 1993 (E&E, 1993). The supplemental human health risk assessment identified the following potential human health risks:

- Consumption of fish from Plow Shop Pond contaminated with arsenic and mercury
- Direct contact with Plow Shop Pond sediment contaminated with arsenic

The supplemental risk assessment indicated that the potential cancer health risks (unmodified to account for the uncertainty associated with arsenic) to a recreational fisherman or family member who regularly consumes fish from Plow Shop Pond ranged from 3×10^{-6} to 4×10^{-4} . Direct contact with sediment presented cancer risks (also unmodified to account for the uncertainty associated with arsenic) ranging from 2×10^{-5} to 2×10^{-4} (under current land use) and 9×10^{-5} to 6×10^{-4} (under future land use). Arsenic accounted for approximately 96 to 99 percent of the total cancer risks. Mercury presented noncancer risks above the regulatory guideline of one (hazard quotients [HQs] range from 2 to 7) to regular consumers of Plow Shop Pond fish. One additional chemical of potential concern (COPC), DDE, presented a cancer risk of 2×10^{-6} , which represents only 0.4 to 4 percent of the total risk.

As discussed in the RI Addendum Report, the risk estimates associated with arsenic are thought to overestimate the true risks. The USEPA Integrated Risk Management System (IRIS) file (December 1993) on inorganic arsenic states that

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"the uncertainties associated with ingested arsenic are such that estimates could be modified downwards as much as an order of magnitude, relative to risk estimates associated with most other carcinogens." If a modifying factor of 10 were applied to the unmodified risk estimates for the fish ingestion and sediment contact pathways, the modified cancer risk estimates would be within or below the Superfund target risk range of 1×10^{-6} to 1×10^{-4} .

1.4.2 Summary of Ecological Risk Assessment

A supplemental ecological risk assessment was performed in the RI Addendum Report (ABB-ES, 1993b) to update the ecological risk assessment of the RI Report (E&E, 1993). The supplemental ecological risk assessment integrated information gathered from several phases of investigation at Plow Shop Pond in order to determine whether environmental contaminants may pose a risk to ecological receptors.

When analyte concentrations were compared to available sediment quality guidelines in the aquatic receptor risk assessment, the average exposure HQ for arsenic was 14.2, whereas the reasonable maximum exposure (RME) HQ for this analyte was 97. Average exposure and RME HQs for the other landfill-related analytes ranged from 1.5 to 128. Plow Shop Pond sediment COPCs not related to the landfill were also present in concentrations in excess of their Reference Toxicity Values (RTVs). HQs ranged from slightly higher than 1, to an RME HQ of 867 for mercury. The RME HQs for cobalt, cadmium, chromium, copper, lead, and zinc were also greater than 1, and ranged from 1.1 (cobalt) to 125 (chromium). For aquatic receptors, approximately 15% of the average exposure hazard index (HI) for Plow Shop Pond is attributable to landfill-related analytes in sediments. The remaining 85% of the average exposure HI is due to analytes from sources other than the Shepley's Hill Landfill, with mercury being the primary risk contributor.

For semi-aquatic wildlife, food web modeling of exposure to RME concentrations of arsenic in Plow Shop Pond sediment and fish tissue resulted in HQs greater than 1 for four of the eight receptor species evaluated in the food web model, including the mallard duck, painted turtle, green frog, and muskrat. Only the mallard duck was at risk from the average scenario. One other landfill-related contaminant (manganese) had an HQ in excess of 1; RME to manganese resulted in an HQ of 5 for the mink. Average and RME exposure to mercury and

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chromium, both sediment COPCs not related to the landfill, were also presumed to result in risks to semi-aquatic receptors, with HQs greater than 1 for the great blue heron, muskrat, mallard, mink, painted turtle, and green frog.

Although the risk assessment findings suggest that contaminants in Plow Shop Pond may be posing a risk to aquatic and semi-aquatic receptors, other ecological data were inconclusive. A total of 193 fish representing seven families and 12 species were collected in Plow Shop Pond as part of supplemental RI activities. Top predators, including the largemouth bass and chain pickerel, represented more than 10% of the total numbers of animals collected. Omnivores and insectivores were also well represented in Plow Shop Pond. Based on the data collected in this study, the species composition and taxa richness of Plow Shop Pond is typical of a southern New England warm water fish community. A gross pathological examination of fish from Plow Shop Pond suggested that the individuals from the population examined are healthy. No tumors, lesions, or other significant abnormalities were observed in any fish examined.

A macroinvertebrate sampling program at Plow Shop Pond was undertaken to provide baseline information regarding the biota associated with aquatic habitats in Plow Shop Pond. Although the macroinvertebrate community data suggest that Plow Shop Pond may be slightly impacted relative to the reference pond, considerable uncertainty was associated with the interpretation of the results of the macroinvertebrate study. Limited numbers of samples, uncertainties associated with the selected reference pond, differences in habitat types between ponds, and natural environmental stochasticity made it difficult to draw conclusions concerning the effect of Plow Shop Pond sediment contaminants. A statistical analysis between sediment chemistry data and macroinvertebrate abundance was generally inconclusive.

1.5 DATA NEEDS

The USEPA document *Managing Contaminated Sediments: EPA Decision Making Process* (USEPA, 1990) outlines six categories of management activities relating to contaminated sediments:

1. Finding contaminated sediments - Identification and monitoring

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2. Assessment of contaminated sediments - Determining the effects of sediment contamination on the environment
3. Prevention and source controls
4. Remediation - Determining when, how, and to what degree contaminated sediment should be remediated
5. Treatment of removed sediments
6. Disposal of removed sediments

Previous studies of Plow Shop Pond have identified contaminants and assessed their effects through human health and ecological risk assessment (i.e., Steps 1 and 2). The draft FS for the Shepley's Hill Landfill Operable Unit and RI/FS activities for Grove Pond and the former Hartnett tannery addresses or will address controls to prevent further contamination of Plow Shop Pond sediments (Step 3). The next decision step for Plow Shop Pond involves deciding whether and to what extent contaminated sediments should be remediated (Step 4). This work plan proposes a series of studies designed to facilitate that decision making process.

The ecological risk estimates presented in the RI Addendum Report suggested that potential adverse effects associated with contaminated sediment exposure may occur to both aquatic and semi-aquatic receptors in Plow Shop Pond. Although risk estimates based upon comparison of inorganic contaminant concentrations to sediment quality screening values were extremely high, obvious impacts to either the macroinvertebrate or fish community were not apparent. The discrepancy between field observations and ecological risk estimates confounds the remedial decision making process. If contaminants are present but are not bioavailable, then the exposure pathway may be incomplete, and remediation of sediment contamination may not be warranted. Site-specific information regarding sediment toxicity and bioavailability would help to reduce the uncertainties associated with the ecological risk assessment and with the development of Preliminary Remediation Goals (PRGs) at Plow Shop Pond.

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The following sampling and evaluation activities are proposed to help resolve issues of bioavailability and risk, and ultimately to determine whether and to what extent sediment remediation will be implemented:

- Measuring concentrations of metals of potential concern in Plow Shop Pond whole sediment, and in sediment elutriate
- Measuring acid volatile sulfide (AVS) and simultaneously extractable metal (SEM) concentrations in Plow Shop Pond sediment
- Measuring methyl mercury and total mercury concentrations in sediment and macroinvertebrate tissue samples from Plow Shop Pond
- Conducting a phased sediment toxicity testing program on sediment and sediment elutriate samples from Plow Shop Pond
- Performing supplemental macroinvertebrate study activities at Plow Shop Pond
- Reviewing and further assessing the relationship between arsenic and mercury contamination in sediment and fish tissue, and human health risks.
- Using uncertainty analysis to further characterize the relationship between mercury contamination in sediment and fish tissue and human health risks.
- Evaluating the effectiveness of institutional controls (such as the posting of Plow Shop Pond) to reduce human health risks.
- Reviewing and refining the ecological risk findings at Plow Shop Pond.

Objectives and sampling design for each of these studies are discussed in Section 3.0.

2.0 GENERAL FIELD INVESTIGATION TASKS

This section describes the general tasks necessary to undertake and complete the site-specific tasks set forth in Section 3.0. The tasks proceed from planning, through field and laboratory work, and data evaluation.

2.1 PROJECT PLANS

Project planning begins prior to beginning field investigation work, and continues throughout the project in response to changing conditions and preliminary data interpretation.

Detailed discussions of relevant requirements, methods, and procedures are presented in this Work Plan and separately in the ABB-ES Fort Devens Project Operations Plan (POP), which includes elements of the Field Sampling Plan (FSP), the Quality Assurance Project Plan (QAPjP), and the Health and Safety Plan (HASp) (ABB-ES, 1993a). The POP contains the major elements of an FSP, in that program-specific procedures for investigation activities are described in detail as these activities are common to investigations that will be conducted at the installation. The POP is a working document that is revised as ABB-ES procedures change and emerging health and safety issues are addressed.

With the exception of detailed AOC-specific activities, the POP includes the QAPjP and elements of the FSP. The POP presents detailed descriptions and discussions of the following elements:

- Project Organization and Responsibilities
- Quality Assurance (QA) Objectives for Measurement
- General Sampling Procedures
- Sample Handling and Custody Procedures
- Equipment Calibration and Preventive Maintenance
- Analytical Procedures
- Data Management
- Internal Quality Control (QC)
- QA Activities
- Problem Prevention

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- Data Assessment Procedures
- Corrective Actions
- Reports
- Site-Specific HASP

2.2 DATA QUALITY OBJECTIVES

Establishing data quality objectives (DQOs) is necessary to establish the level of detail required for proposed field investigation activities. Data generated during the field and laboratory tasks will be used to characterize sediment and to assess the bioavailability and toxicity of sediment contaminants. These data will be used to assist in developing and evaluating remedial alternatives for the Plow Shop Pond Operable Unit. The levels of data quality, USAEC Certification Classes, and DQOs for the project are specified in Volume I, Subsection 3.2 of the POP.

On-site field measurement of pH, oxidation/reduction potential (ORP), and temperature will conform to the guidelines presented in Volume 1, Subsection 4.6 of the POP. Field measurement data will be considered representative of USEPA Level II data quality.

Data from off-site laboratory analysis of AVS, SEM, TOC, and other parameters for which USAEC performance demonstration is not required will be considered representative of USEPA Level III data quality.

Data from off-site laboratory analysis of inorganics in sediment will be considered representative of USEPA Level IV data quality.

2.3 FIELD INVESTIGATIONS

Fieldwork will be conducted in accordance with the procedures specifically identified in Volume I, Section 4.0 of the POP, or this Work Plan. A key controlling document for the methods and procedures used in conducting the field investigations will be *Geotechnical Requirements for Drilling, Monitor Wells, Data Acquisition, and Reports* (USATHAMA, 1987). This document has been reviewed and its standard techniques have been included in the POP. Site-specific conditions, plans, and rationale are presented in Section 3.0 of this Work Plan.

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The tasks necessary to undertake and complete the field investigation program are described in the following subsections.

2.3.1 Mobilization

Following authorization to begin fieldwork, ABB-ES and its subcontractors will mobilize to Fort Devens and implement the proposed field investigation program.

Mobilization will consist of field personnel orientation and equipment mobilization, and will take place before initiation of the field program. A field team orientation meeting will be held with ABB-ES personnel and subcontractors to familiarize on-site personnel with the site history, health and safety requirements, Fort Devens security requirements, and USAEC field procedures. Equipment mobilization will include, but will not be limited to, the transportation and setup of the following equipment:

- subcontractor equipment and necessary materials and supplies
- health and safety and decontamination equipment
- sediment sampling equipment
- survey equipment

2.3.2 Site-Specific Field Investigation Tasks

The plans and rationale for site-specific field investigations, including analytical requirements, are described in detail in Section 3.0 of this Work Plan. Performing those investigations will involve combinations of the following tasks:

- *in situ* measurement of sediment pH, ORP, and temperature
- sediment sampling
- surveying

These tasks will be performed in accordance with the procedures presented in Volume I, Section 4.0 of the POP, or this Work Plan.

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2.4 LABORATORY ANALYTICAL PROGRAM

The laboratory analytical program is designed to measure the concentration of inorganic contaminants of concern in bulk sediment, as well as to collect chemical data to assess bioavailability of those analytes. The 12 inorganic contaminants of concern are: mercury, chromium, manganese, arsenic, lead, barium, iron, cadmium, zinc, nickel, copper, and cobalt.

The proposed laboratory analytical program for Plow Shop Pond includes the above inorganics, TOC, and percent solids. Off-site laboratory analytical procedures are presented in Volume 1, Section 7.0 of the POP (ABB-ES, 1993a). The laboratory QA Plan and USAEC Certified Analytical Methods are presented in Volume II of the POP, Appendices B and C, respectively. Analysis for AVS and SEM will be according to the USEPA *Draft Analytical Method for Determination of Acid Volatile Sulfide in Sediment* (USEPA, 1991) (Appendix A).

2.5 QUALITY ASSURANCE/QUALITY CONTROL

Environmental sampling and analysis will be conducted in accordance with requirements of the USAEC QA Program (USATHAMA, 1990) and the POP. QC procedures established for ABB-ES' field activities include the use of calibration standards and blanks for pH, specific conductance, temperature, and photoionization meter measurements.

Details of the collection procedures and frequency of the QC samples are provided in Volume I, Section 9.0 of the POP. QA/QC samples typically submitted to the laboratory include duplicate samples, trip blanks, and equipment rinsate blanks. Duplicate samples are collected from 5 percent of all samples collected and analyzed for the same parameters as the sample that was duplicated. Trip blanks are collected (one per shipment) and shipped with all coolers containing water samples to be analyzed for VOCs. These provide a basis for assessing the potential for contamination of samples with VOCs during sample collection or shipment. Rinsate blank samples are collected from sampling equipment to address the potential for cross-contamination. The rinsate blanks will be analyzed for PAL parameters, as appropriate. Five percent matrix spike and matrix spike duplicates are analyzed to characterize matrix effects. Methods

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requiring surrogates do not require matrix spikes. Method blank samples will also be analyzed to maintain internal QA/QC at the laboratory.

Samples will be handled and conveyed to the subcontractor laboratory in accordance with specified chain of custody (COC) procedures. Sample management procedures, including sample container preservation requirements, COC program protocol and records, analytical request forms, and sample tracking and shipping are described in Volume I, Section 5.0 of the POP. ABB-ES will receive QA packages for all samples from the subcontractor laboratory and will independently review them.

While analyses are being conducted, the subcontractor laboratory QA Coordinator will provide the ABB-ES QA Supervisor with the documentation specified in Volume I, Subsection 7.3 of the POP. The subcontractor laboratory will supply copies of all corrective actions to ABB-ES for approval. Although the subcontractor laboratory controls laboratory operations, the ABB-ES QA Supervisor retains ultimate responsibility for data quality.

2.6 PHYSICAL PARAMETERS

Grain-size distribution will not be established for sediment samples from Plow Shop Pond. Samples for determination of grain-size distribution were collected as part of supplemental RI sampling.

2.7 DATA MANAGEMENT

Geotechnical, biological, and chemical data generated as part of these field investigations will be managed in accordance with applicable USAEC data management procedures (discussed in Volume I, Section 8.0 of the POP). Data for this project will include the results of chemical analyses of biological and sediment samples, as well as the results of the sediment toxicity test program.

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2.8 DATA EVALUATION

ABB-ES will evaluate data generated from the field investigations to confirm whether they meet specified DQOs, and to assess whether data gaps have been adequately filled. Interpretation of the data will be part of the basis for deciding whether and to what extent contaminated sediments at Plow Shop Pond should be remediated. Completed field investigations and resulting data will be documented in the FS Report for the Plow Shop Pond Operable Unit.

3.0 SITE SPECIFIC SUPPLEMENTAL SAMPLING ACTIVITIES

This section presents the site-specific objectives and sampling design for supplemental sampling activities at Plow Shop Pond. A summary of the proposed sampling and analysis activities described in this work plan is presented in Table 1.

3.1 SEDIMENT SAMPLING

The primary objective of the supplemental sediment sampling program in Plow Shop Pond is to characterize the bioavailability and toxicity of inorganic contamination in the pond's sediments. The proposed assessment of speciation of mercury and evaluation of AVS and SEM will provide additional information regarding the partitioning, toxicity, fate, and transport of these analytes in Plow Shop Pond sediments. Evaluation of sediment/elutriate chemistry will provide a means of assessing sediment toxicity to aquatic ecological receptors.

Proposed sediment sampling and analysis activities include collection of shallow sediment samples from 22 locations established in a systematic grid in Plow Shop Pond (Figure 2). These locations were selected to represent a broad distribution of contaminants and concentrations. Fifteen of these locations correspond to sediment locations sampled during supplement RI activities. Sediment sampling stations will be field located with an electronic distance meter (EDM) or a Global Positioning System (GPS) and temporarily marked with buoys. Pond water depths will be recorded at each sediment sampling station. Shallow sediment samples will be collected in accordance with Volume I, Subsection 4.5.3, of the POP (ABB-ES, 1993a).

The proposed sediment sampling and analysis activities focus on the 12 inorganic contaminants of concern identified in the ecological and human health risk assessments in the RI Addendum Report (ABB-ES, 1993b); analyses for the remaining PAL metals, pesticides, and PCBs are not proposed. The bulk sediment samples will be analyzed for the following 12 PAL metals: arsenic, barium, cadmium, chromium, cobalt, copper, iron, lead, manganese, mercury, nickel, and zinc. These 12 inorganic analytes were the primary ecological and human health risk contributors evaluated in the RI Addendum Report risk

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assessment (ABB-ES, 1993b). The sediment samples will also be analyzed for TOC, SEM, AVS, grain size distribution, and percent solids.

Elutriate from 10 of the sediment samples will be analyzed for the same 12 PAL inorganics (arsenic, barium, cadmium, chromium, cobalt, copper, iron, lead, manganese, mercury, nickel and, zinc. These 10 sediment samples will also be evaluated for total mercury and methylmercury in both whole sediment and elutriate water samples. Table 2 identifies locations for elutriate and methyl mercury analysis. The 10 sample locations were selected to represent a broad range of sediment concentration, as well as to provide good spatial coverage of the pond.

Elutriate will be prepared by passing sediment through a 2.0 mm stainless steel sieve, and then adding the screened material to dilution water at a sediment to water ratio of 1:4. After stirring the resultant slurry for 30 minutes, the mixture will be allowed to settle for 1 hour. The resultant supernatant will be siphoned and centrifuged. No filtration will occur, and fine-grained sediment particles may be present in the resultant elutriate.

Sulfide, a common constituent of pond sediments, forms insoluble precipitates with 9 of the 12 inorganics identified as contributors to aquatic receptor risk: cadmium, cobalt, copper, iron, lead, manganese, mercury, nickel, and zinc. In addition, organic compounds in Plow Shop Pond may chelate the metals, either preventing them from being released from the sediments, or lowering bioavailability of metals that are not trapped in the sediments. Molar concentrations of AVS will be determined in all of the sediment samples to address the partitioning of inorganics between the solid sediment phase and the interstitial pore water.

Information derived from the proposed sediment sampling program at Plow Shop Pond may be used to evaluate risks to ecological and human receptors, to help derive PRGs and/or target cleanup levels for contaminated sediments within Plow Shop Pond, and to help monitor or evaluate the success of any remedial actions at Plow Shop Pond.

3.2 SEDIMENT LABORATORY BIOASSAYS

A phased laboratory bioassay program is proposed to assess the toxicity of sediments to aquatic organisms residing within the sediments (i.e., benthic and infaunal receptors). Information derived from the proposed bioassays at Plow Shop Pond may be used to help derive PRGs and/or target cleanup levels for contaminated sediments within Plow Shop Pond, and to help monitor or evaluate the success of any remedial actions at Plow Shop Pond. Information derived from the laboratory bioassay program will be used in a "weight-of-evidence" approach to reduce the uncertainties associated with the ecological risk assessment in the aquatic systems at the Plow Shop Pond Operable Unit.

Although the results of the toxicity tests will be used to predict the effects that might occur to aquatic ecological receptors *in situ*, it is important to recognize that: (1) exposure to contaminated sediments might be avoided by motile organisms; and, (2) toxicity to organisms *in situ* may be dependent upon sediment physical characteristics and equilibrium partitioning that are not duplicable under laboratory conditions (ASTM, 1993). In order to cost-effectively evaluate the toxicity of sediments in Plow Shop Pond, a phased bioassay study is proposed. If information obtained in earlier phases of the bioassay is sufficient to meet study objectives, latter phases of bioassay investigation will not be implemented.

Phase I: Screening Level Bioassays

The objective of the Phase I screening level bioassays is to obtain laboratory data to evaluate adverse effects associated with exposure of the freshwater invertebrate species *Ceriodaphnia dubia* to sediment elutriate, and *Chironomus tentans* and *Hyallella azteca* to whole sediment. Twenty-two short-term chronic toxicity tests with *C. dubia* and *C. tentans* are proposed to provide a screening level spatial distribution of sediment toxicity in Plow Shop Pond. Endpoints to be evaluated in the proposed short-term chronic test include survival, growth, and reproduction. Twenty-two sediment samples for screening level bioassay will be collected concurrently and from the same locations as the sediment samples collected for analytical chemical analyses.

Ceriodaphnia dubia or water fleas are small crustaceans that are easily cultured under laboratory conditions and have a short generation time. *C. dubia* survival and reproductive data are easily obtainable in sediment toxicity tests; furthermore,

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a substantial database exists detailing the sensitivity of *C. dubia* to various contaminants (ASTM, 1993). *C. dubia* in whole sediment tests are thought to be exposed to both water soluble and sediment-sorbed contaminants in overlying water and surface sediments. They are important components of aquatic food webs and may play a role in food chain transfer of inorganics in Plow Shop Pond (ASTM, 1993). The proposed 7-day subchronic *C. dubia* test will evaluate survival and reproduction of this species. The reproductive endpoint evaluated for *C. dubia* will be the observed number of offspring/female/day.

Larvae of the chironomid midge (*Chironomus tentans*) are frequently used in sediment toxicity testing because they are relatively large, are easily cultured under laboratory conditions, have a short generation time, and they have direct contact with sediment (ASTM, 1993). *C. tentans* are sensitive to many contaminants associated with sediments. Midge larvae are important dietary components of fish and surface-feeding ducks, and play an important role in sediment contaminant cycling. *C. tentans* burrow into sediment and build a protective case; this exposure to sediments makes them a reasonable test species to evaluate benthic communities in Plow Shop Pond. The proposed 10-day subchronic *C. tentans* study will evaluate survival of *C. tentans* larvae.

Following statistical analysis, the survival and reproductive no observed effect concentration (NOEC) and lowest observed effect concentration (LOEC) will be calculated for *C. dubia*. Survival of *C. tentans* will be statistically compared with survival of control organisms to assess the toxicity of sediments to midge larvae.

To provide additional characterization of potential sediment toxicity, the Army will perform a 10-day survival test using *Hyallella azteca* in accordance with guidance provided by USEPA in the draft document *Methods for Measuring the Toxicity and Bioaccumulation of Sediment-associated Contaminants with Freshwater Invertebrates* (USEPA, 1994). *H. azteca* is an epibenthic detritivore that burrows near the sediment surface and ingests sediment particles. Because *H. azteca* requires at least 35 days to reproduce, only survival will be measured with this species. The proposed *H. azteca* bioassays will be conducted with sediment collected from the 10 sediment sampling locations proposed for analysis for methylmercury (see Table 2).

If the results of the Phase I bioassay program indicate that minimal sediment toxicity exists in Plow Shop Pond (i.e., if little or no statistically significant toxicity to test organisms is observed following subchronic exposure to whole sediment samples) no further bioassay studies are proposed. However, if the results indicate that exposure to certain sediment samples results in significant effects on the growth, reproduction, or survival of test species, then Phase II toxicity testing is proposed.

Phase II: Whole Sediment Dilution Series Bioassays

Based upon a preliminary analysis of the results of the Phase I bioassay program at Plow Shop Pond, a limited dilution series bioassay study may be conducted using a subset of 3 to 5 sediment samples from the original collected samples. The dilution experiments will be used to calculate NOECs and LOECs (and if necessary the median lethal concentration [LC_{50}]) to the test species evaluated in the Phase I investigation (i.e., *C. dubia* and *C. tentans*). The dilution series will employ whole sediment from the selected stations diluted with a range of reference sediment from a portion of Plow Shop Pond. Potential sediment dilutions include 100%; 50%; 25%; 12.5%; and, 6.25%; however, the lower range of dilutions may not be required if NOECs and LOECs are determined at the higher end of the range. The reference sediment will be defined as Plow Shop Pond sediment with minimal demonstrated toxicity, as determined in the Phase I screening level bioassay. Use of nontoxic Plow Shop Pond sediment as the reference sediment for the bioassay program will address the identified uncertainties associated with the reference pond used in the supplemental RI (ABB-ES, 1993b).

Following statistical analysis, survival and reproductive NOECs and LOECs will be calculated for *C. dubia* for each sample evaluated in the dilution series. *C. tentans* survival will be statistically compared with survival of control organisms to assess the toxicity of whole sediment to midge larvae.

The results of the sediment dilution series may be used to help establish PRGs for Plow Shop Pond sediment, and to help define the sampling locations for the Phase III sediment bioassay investigation. If possible, a dose-response curve will be developed to facilitate setting of PRGs.

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Phase III: Interstitial Water Toxicity Identification Evaluation

The Toxicity Identification Evaluation (TIE) is a procedure for evaluating the toxicity of sediments using sediment interstitial water. Strong correlations are known to exist between contaminant concentrations in interstitial pore water and observed effects on macroinvertebrates exposed to sediment-associated contaminants (Ankley and Thomas, 1992). Because the physical and toxicological characteristics of elutriate water are generally similar to sediment pore water, and collection of elutriate water is considerably less labor-intensive than collection of pore water, elutriate water prepared from Plow Shop Pond sediments will be used in the Phase III TIE investigation.

The Phase III approach will combine the quantification of elutriate water toxicity with TIE procedures in order to identify and quantify contaminants responsible for sediment toxicity. Fractionation procedures will be used to identify toxic constituents in the heterogenous mixtures of contaminants that characterize Plow Shop Pond. Three to four toxicity tests will be performed on elutriate using either a 48 hour static acute toxicity test or a short-term chronic toxicity test with *C. dubia*.

To isolate toxic contaminants from Plow Shop Pond sediment, sample manipulations and subsequent fractionation techniques will be used in combination with toxicity tracking tests (Ankley and Thomas, 1992). Fractionation steps will consist of a series of sample manipulations to identify physical and chemical properties of, and relationships among, the toxicants. This approach will allow direct relationships to be established between toxicants and measured analytical data. Use of the TIE approach will help elucidate antagonistic and synergistic interactions, as well as sediment matrix effects. An overview of the TIE sample manipulations and fractionation techniques that may be used in the Plow Shop Pond TIE is presented in Figure 3.

Based upon the results of the TIE, major contributors to sediment toxicity in Plow Shop will be identified. Site-specific numerical criteria for contaminants in Plow Shop Pond sediment pore water will be identified if possible. These site-specific criteria will be used to help establish PRGs or target cleanup levels for Plow Shop Pond sediment.

Phase IV: Confirmatory Phase Spiked Bioassays

After suspected toxicants are isolated through the Phase III TIE procedures, a confirmatory phase of bioassay work is proposed. Confirmation of the Phase III TIE approach is critical in order to ensure that the manipulations of sediment used in the TIE partitioning did not create artifacts that could effect study conclusions (Ankley and Thomas, 1992). The Phase III confirmatory phase of work may involve correlation analysis and spiked sediment toxicity testing.

For correlation analyses, observed toxicity from the Phase I-III toxicity analyses may be regressed against expected toxicity due to measured concentrations of suspected toxicants. This approach may be used to generate data concerning the additive, synergistic, and antagonistic effects of the contaminants.

For the purpose of spiked sediment toxicity testing, reference sediments will be defined as Plow Shop Pond sediment with minimal demonstrated toxicity, as evaluated in the Phase I and II screening level bioassay. These reference sediments will be spiked in the laboratory with known concentrations of the suspected toxicants. As in the Phase I screening level bioassay, adverse effects associated with subchronic exposure of sediment to *C. dubia*, *C. tentans*, or *H. azteca* will be evaluated. A maximum of 4 spiked sediment toxicity tests with each test species is proposed. Results from the spiked sediments will be compared with results obtained from control or reference sediments to identify toxic concentrations of contaminants.

The confirmatory spiked sediment bioassays will be used to measure the effects of specific chemicals and to analyze causality. Concentrations at which toxicity occurs in spiked Plow Shop Pond sediment may be used to help establish PRGs or target cleanup levels.

3.3 SUPPLEMENTAL MACROINVERTEBRATE STUDY

A supplemental macroinvertebrate study at Plow Shop Pond is proposed to provide additional information regarding the biota associated with aquatic habitats at Plow Shop Pond, and to provide information for possible use in evaluation of effects and effectiveness of any future remedial actions. The primary objective of the supplemental macroinvertebrate study is to evaluate the relationship(s)

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between sediment contamination and gross morphological deformities associated with certain benthic macroinvertebrate taxa.

A number of studies have suggested that deformities in chironomid midge (Diptera: Chironomidae) larvae may serve as sensitive indicators of environmental pollution (e.g., Weiderholm, 1984; Cushman, 1984; and, Warwick, 1987). Larvae from polluted sediments have been demonstrated to show greater frequency of mouthpart deformities than larvae from cleaner sediments. The proposed study would involve an evaluation of gross mentum deformities in approximately 150 to 200 archived chironomid midge larvae collected during the supplemental RI of Plow Shop Pond (ABB-ES, 1993b). Mounted specimens will be examined at 100-400X magnification (Cushman, 1984); gross deformities of the mentum will be evaluated in larvae from Plow Shop Pond and New Cranberry Pond (the reference pond). If sufficient data are generated, differences between the percentages of deformed chironomids in Plow Shop Pond sediment and in the reference pond will be evaluated statistically.

Information from this aspect of the supplemental macroinvertebrate study may be used to characterize the existence and extent of ecological impairments, evaluate the effectiveness of remedial actions, and provide a baseline characterization of the effects related to inorganic pollutants in Plow Shop Pond sediment.

3.4 MACROINVERTEBRATE TISSUE ANALYSIS FOR MERCURY

Mercury levels in largemouth bass tissue from Plow Shop Pond exceeded the U.S. Food and Drug Administration (USFDA) action level of 1.0 milligram per kilogram (mg/kg) (ABB-ES, 1993b). However, no information is available regarding mercury concentrations in other biota within the pond. A limited evaluation of mercury in benthic macroinvertebrates is proposed to better understand the cycling of mercury in Plow Shop Pond.

To provide information on food chain uptake, macroinvertebrate taxa will be collected for tissue analyses. Benthic macroinvertebrates will be collected at three stations co-located with sediment and sediment elutriate sampling stations. Macroinvertebrate collection stations have been tentatively identified at SHD-94, -10, -13, and -19 (see Figure 2). Organisms will be collected with a grab sampler

or a dip net, sieved with a Number 30 standard sieve, and transferred to Teflon vials. Samples will be frozen and analyzed for total mercury and methylmercury.

The Army will supplement analysis of collected macroinvertebrate tissue with three 28-day uptake studies conducted in the laboratory using Lumbricus variegatus.

3.5 SUPPLEMENTAL EVALUATION OF MERCURY ACCUMULATION IN SEDIMENTS AND FISH TISSUE

The human health risk estimates presented in the RI Addendum Report suggested that mercury in Plow Shop Pond fish may pose health risks in excess of USEPA risk management guidelines. The uncertainties associated with estimating fish consumption risks are sufficient to warrant a quantitative uncertainty analysis.

An uncertainty analysis would be particularly helpful in interpreting and managing the human health risks in the FS:

- While the maximum detected concentration (4 parts per million [ppm]) of mercury in Plow Shop Pond bullheads and bass exceeds the USFDA action level for mercury in fish of 1 ppm, the average concentration (1.144 ppm) approximates it.
- The HI values associated with the mercury in Plow Shop Pond fish ranged from two to seven; these are within an order of magnitude of USEPA's target HI of one.

Further clarification of the significance of these findings through an uncertainty analysis would allow for a bracketing of the risk estimates. Instead of relying on point estimates of risk, an uncertainty analysis using Monte Carlo sampling would be used to develop a distribution of the risk estimates. Sample output from such an analysis would be: "there is a 75% chance that the HI for fishermen who consume Plow Shop Pond fish is less than 1.3". ABB-ES would use an available software package to generate the probability distributions.

If sediment remediation were to be undertaken to reduce the health risks from fish consumption, it will be necessary to understand the dynamics between

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removal of sediment and fish tissue impacts. The correlation between sediment removal and fish tissue levels is critical in setting sediment cleanup goals. The literature will be reviewed to determine the effectiveness of sediment removal in reducing fish tissue contaminant levels.

4.0 PROJECT MANAGEMENT

The project organization structure is illustrated in Figure 4. Solid lines on the figure depict direct lines of control while dotted lines indicate channels of communication. Rationale for project organization and resource allocation are discussed in the POP. QA/QC procedures and responsibilities for ABB-ES, USAEC, and laboratory personnel are also described in the POP.

4.1 PROJECT MANAGEMENT

The duties, functions, and responsibilities associated with project management are detailed in the following paragraphs.

Program Manager. The Program Manager for ABB-ES' USAEC efforts is Mr. Joseph T. Cuccaro. He is responsible for providing direction, coordination, and continuous monitoring and review of the program. His responsibilities include initiating program activities; participating in work plan preparation; coordinating staff assignments; assisting in the identification and fulfillment of equipment and special resource needs; monitoring all task activities to confirm compliance with schedule, fiscal, and technical objectives; maintaining communications both internally and with the USAEC Contracting Officer's Representative (COR) through continuous interaction, thereby allowing quick resolution of potential problems; providing final review and approval of work plans, task deliverables, schedules, contract changes, and manpower allocations; and developing coordination among management, field teams, and support personnel to maintain consistency of performance.

Project Manager. The Project Manager for ABB-ES' Fort Devens efforts, Mr. Paul Exner, P.E., has the day-to-day responsibility for conducting the Fort Devens project. The Project Manager is responsible for confirming the appropriateness and adequacy of the technical or engineering services provided for a specific task; developing the technical approach and level of effort required to address each element of a task; supervising day-to-day conduct of the work, including integrating the efforts of all supporting disciplines and subcontractors for all tasks; overseeing the preparation of all reports and plans; providing for QC and quality review during performance of the work; confirming technical integrity, clarity, and

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usefulness of task work products; forming a task group with expertise in disciplines appropriate to accomplish the work; reviewing and approving sampling tests and QA plans, which include monitoring site locations, analysis methods to be used, and hydrologic and geophysical techniques to be used; developing and monitoring task schedules; supervising task fiscal requirements (e.g., funds management for labor and materials), and reviewing and approving all invoicing actions; and providing day-to-day communication, both within the ABB-ES team and with the USAEC COR, on all task matters including task status reporting.

Corporate Officer. ABB-ES' Corporate Officer, William R. Fisher, P.E., is responsible for ensuring that a contract for the services to be provided has been executed; necessary corporate resources are committed to conduct the program activities; corporate level input and response is readily available to both the ABB-ES team and the USAEC COR; and assistance is provided to the Program and Project Managers for project implementation.

Technical Director and Project Review Committee. The members of the Project Review Committee for this Task Order are Mr. James Buss, P.G.; Mr. Michael Murphy; and Mr. Jeff Brandow. Mr. Buss will serve as Technical Director and will be responsible for the overall technical quality of the work performed; he also will serve as chairman of the review committee. The function of this group of senior technical and/or management personnel is to provide guidance and oversight on the technical aspects of the project. This is accomplished through periodic reviews of the services provided to confirm that they represent the accumulated experience of the firm, are being produced in accordance with corporate policy, and live up to the objectives of the program as established by ABB-ES and USAEC.

Quality Assurance Supervisor. Mr. Christian Ricardi is the QA Supervisor for ABB-ES' USAEC program and this project. The QA function has been established so that appropriate protocols from USAEC, Commonwealth of Massachusetts, and USEPA Region 1 are followed. In addition, the QA Supervisor must confirm that QC plans are in place and implemented for each element of the task. The QA Supervisor reports directly to the Program Manager, but is responsible to the Project Manager in matters related to management of the QA/QC work element. The QA Supervisor is independent of the Project Manager relative to corrective action. The QA Supervisor has authority to stop work that is not in compliance with the POP, provided he has

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the concurrence of the USAEC Chemistry Branch, the Program Manager, the COR, and the Contracting Officer.

Health and Safety Supervisor. Ms. Cynthia E. Sundquist is the Health and Safety Supervisor for the Fort Devens project, reporting directly to the Project Manager. She has stop work authority to prevent or mitigate any unacceptable health and safety risks to project personnel, the general public, or the environment. Responsibilities of this position include confirming that the project team and, in particular, field personnel, comply with the ABB-ES HASP; helping the Program Manager and Project Manager develop the site-specific HASP; making certain that the HASP is distributed to appropriate personnel; and informing the Program Manager and the appropriate USAEC personnel in the specified manner when any health- or safety-related incident occurs.

Contract Manager. Ms. Elaine H. Findlay is the Contract Manager for the Fort Devens effort. The Contract Manager supports the Program Manager and Project Manager in all contractual matters, providing a liaison between contract representatives for USAEC and all subcontracted services.

Project Administrator. Ms. Tina Clark is the Project Administrator for the Fort Devens effort. The Project Administrator supports the Program Manager and Project Manager in the day-to-day monitoring of fiscal, schedule, and documentation requirements. She is responsible for maintaining the necessary systems to support budget monitoring and controls, and schedule monitoring and maintenance; and for controlling the flow and processing of documentation.

Task Leader. Mr. Stanley Reed will serve as Task Leader for the Plow Shop Pond Supplemental Field Investigation. As a Task Leader, he is responsible for planning all ABB-ES' geologic, hydrogeologic, and ecological investigations. He also is responsible for the interpretation of all chemical and hydrogeologic information and data for the preparation of the Plow Shop Pond Operable Unit FS Report.

Field Operations Leader. Mr. Douglas Pierce will serve as the Field Operations Leader for the Fort Devens Field Program. As Field Operations Leader he is responsible for conducting the field program in accordance with procedures outlined in the Work Plan and POP.

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Laboratory/Data Management Leader. Mr. Tim Dame, as the coordinator of laboratory services, is responsible for implementing and maintaining the Fort Devens analytical program. His responsibilities as the Laboratory Management Leader will include coordination with the Project Manager, QA Supervisor, and the analytical subcontractor on overall project and individual site analytical efforts. As the Data Management Leader, Mr. Dame is responsible for operating and maintaining the database management systems committed to USAEC projects.

4.2 SUBCONTRACTORS

The following services and/or activities will be performed by subcontractors during the Plow Shop Pond field investigation activities: sediment bioassays, laboratory chemical analysis, and surveying.

Sediment Bioassay Services. Sediment bioassays will be subcontracted to Springborn Laboratories, Inc., Wareham, Massachusetts.

Laboratory Chemical Analysis. The primary analytical laboratory for samples collected by ABB-ES at Fort Devens is Environmental Science & Engineering, Inc. (ESE) of Gainesville, Florida. ESE's analytical program is USAEC-approved. Analysis for methylmercury will be done by Frontier Geoscience, Seattle, Washington.

Surveying Services. Martinage Engineering of Reading, Massachusetts, a professional land surveying company registered in the Commonwealth of Massachusetts, will be subcontracted to establish map coordinates for sediment sampling locations. Surveying activities will be coordinated and monitored by the Field Operations Leader, who will keep the Project Manager informed on a day-to-day basis.

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5.0 SCHEDULE

The projected schedule for the Plow Shop Pond Supplemental Investigation is shown in Figure 5. The figure shows the anticipated schedule for conducting field and laboratory activities and for preparing a draft technical report.

GLOSSARY OF ACRONYMS AND ABBREVIATIONS

ABB-ES	ABB Environmental Services, Inc.
AOC	Area of Contamination
AVS	Acid Volatile Sulfide
AWQC	Ambient Water Quality Criteria
COC	chain of custody
COPC	chemical of potential concern
COR	Contracting Officer's Representative
DDD	2,2-bis(para-chlorophenyl)-1,1-dichloroethane
DDE	2,2-bis(para-chlorophenyl)-1,1-dichloroethene
DDT	2,2-bis(para-chlorophenyl)-1,1,1-trichloroethane
DQO	Data Quality Objective
ESE	Environmental Science and Engineering
EDM	Electronic Distance Meter
FS	Feasibility Study
FSP	Field Sampling Plan
ft	foot (feet)
GPS	global positioning system
HASP	Health and Safety Plan
HI	Hazard Index
HQ	Hazard Quotient
IRIS	Integrated Risk Information System
LC ₅₀	median lethal concentration
LOEC	lowest observed effects concentration
mg/kg	milligrams per kilogram
mm	millimeter
NOEC	no observed effects concentration
NPL	National Priorities List

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GLOSSARY OF ACRONYMS AND ABBREVIATIONS

ORP	oxidation/reduction potential
PAH	Polynuclear Aromatic Hydrocarbon
PAL	Project Analyte List
PCB	polychlorinated biphenyl
ppm	parts per million
POP	Project Operations Plan
PRG	Preliminary Remediation Goal
QA	Quality Assurance
QAPjP	Quality Assurance Project Plan
QC	Quality Control
RI	Remedial Investigation
RME	Reasonable Maximum Exposure
RTV	Reference Toxicity Value
SEM	Simultaneously Extractable Metals
TAL	Target Analyte List
TCL	Target Compound List
TIE	Toxicity Identification Evaluation
TOC	total organic carbon
USAEC	U.S. Army Environmental Center
USEPA	U.S. Environmental Protection Agency
USFDA	U.S. Food and Drug Administration
VOC	volatile organic compound

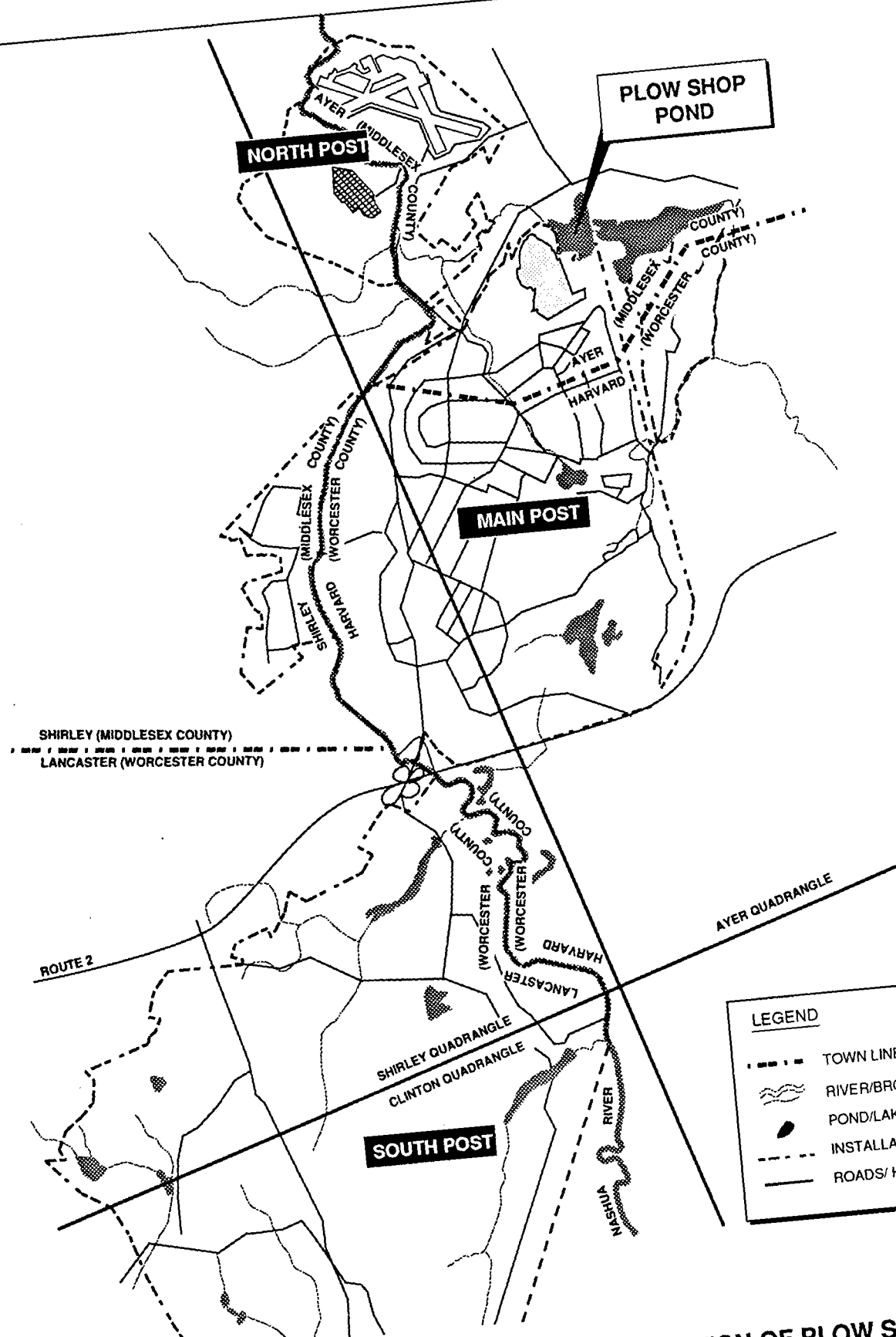
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LEGEND

- TOWN LINE
- ~ RIVER/BROOK
- POND/LAKE
- - - INSTALLATION BOUNDARY
- ROADS/ HIGHWAY

MASSACHUSETTS

FT. DEVENS

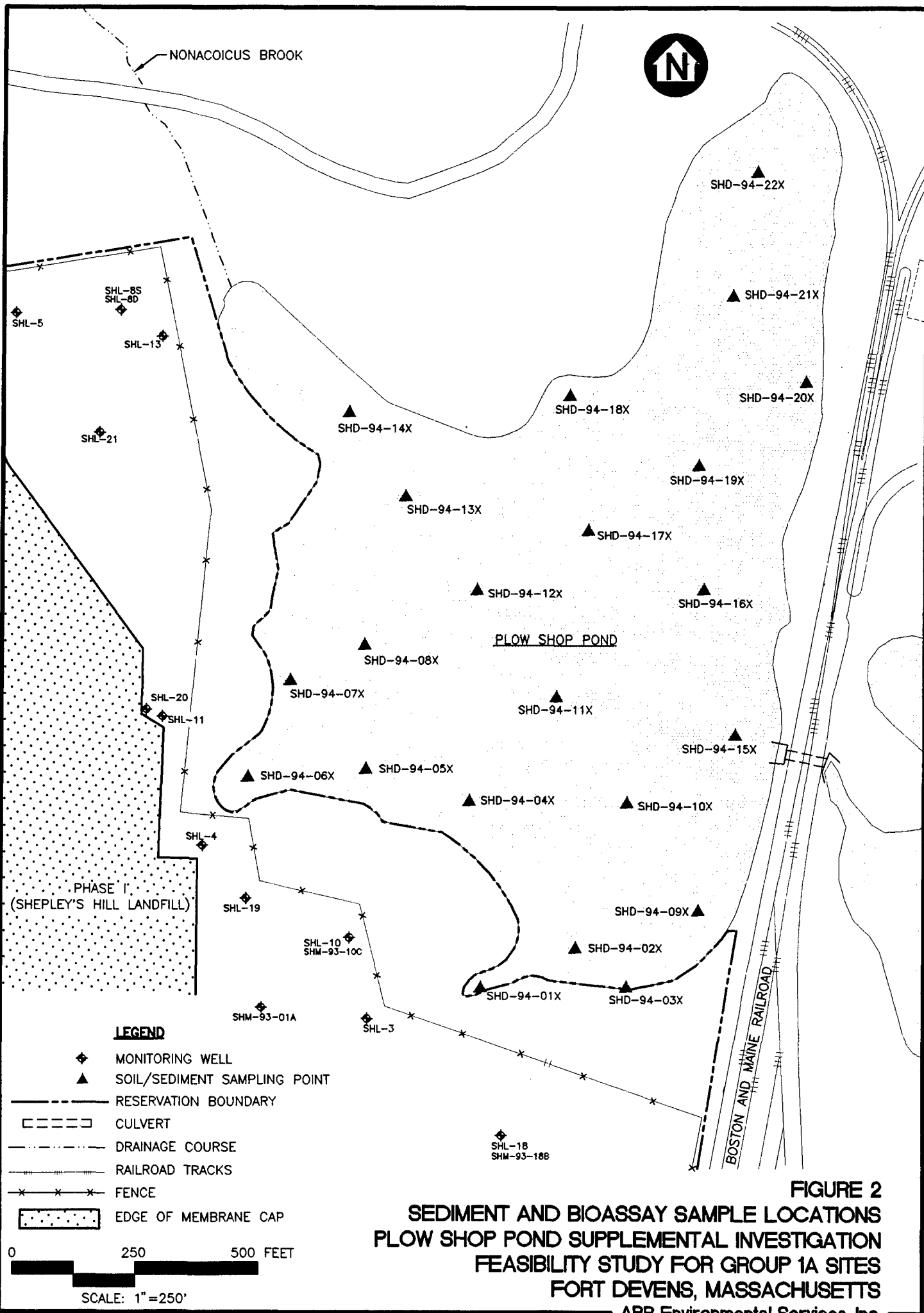
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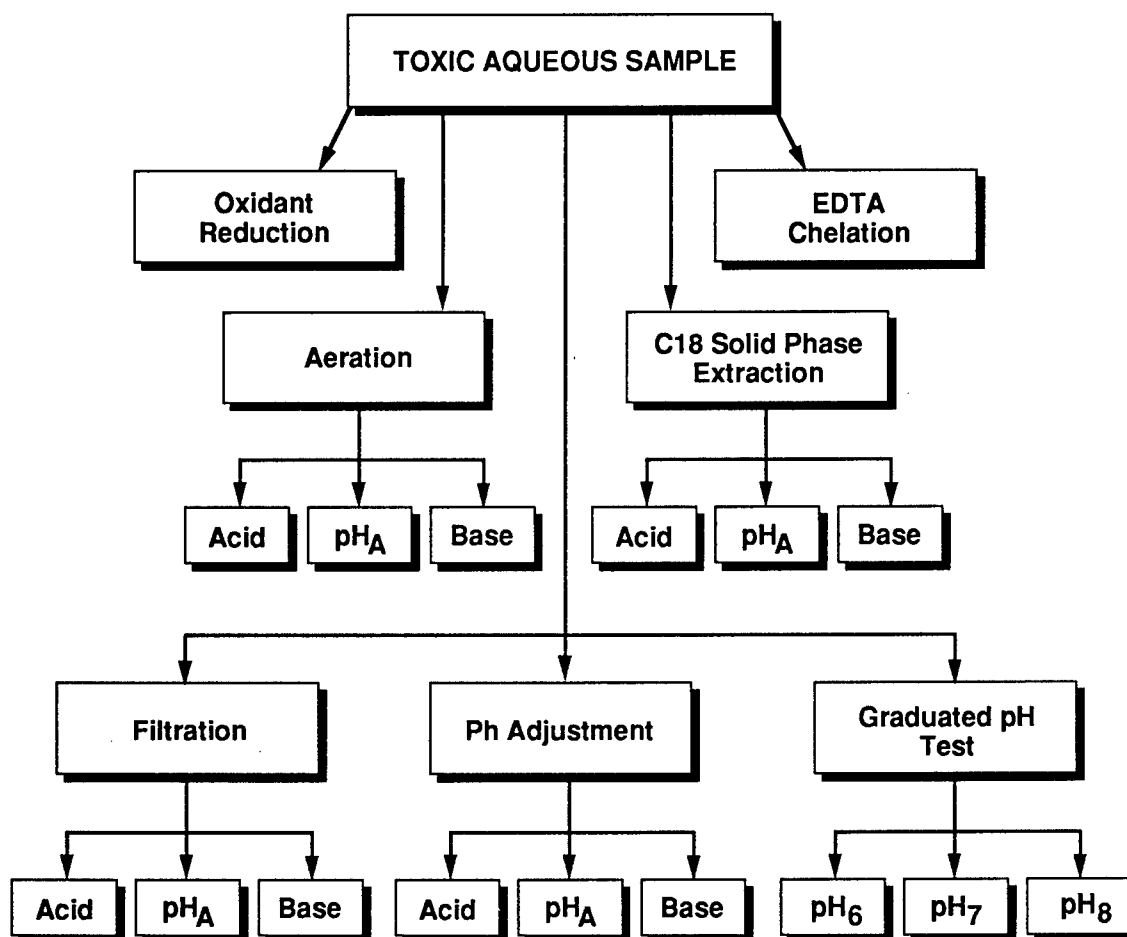
SCALE IN FEET

0 3000 6000

FIGURE 1
LOCATION OF PLOW SHOP POND
PLOW SHOP POND SUPPLEMENTAL INVESTIGATION
FEASIBILITY STUDY FOR GROUP 1A SITES
FORT DEVENS, MA

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NOTE:

pH_A = Ambient pH

Source = USEPA, 1992

EDTA = Ethylenediaminetetraacetic Acid

FIGURE 3
TOXICITY CHARACTERIZATION PROCESS
FLOW SHOP POND SUPPLEMENTAL INVESTIGATION
FEASIBILITY STUDY FOR GROUP 1A SITES
FORT DEVENS, MA

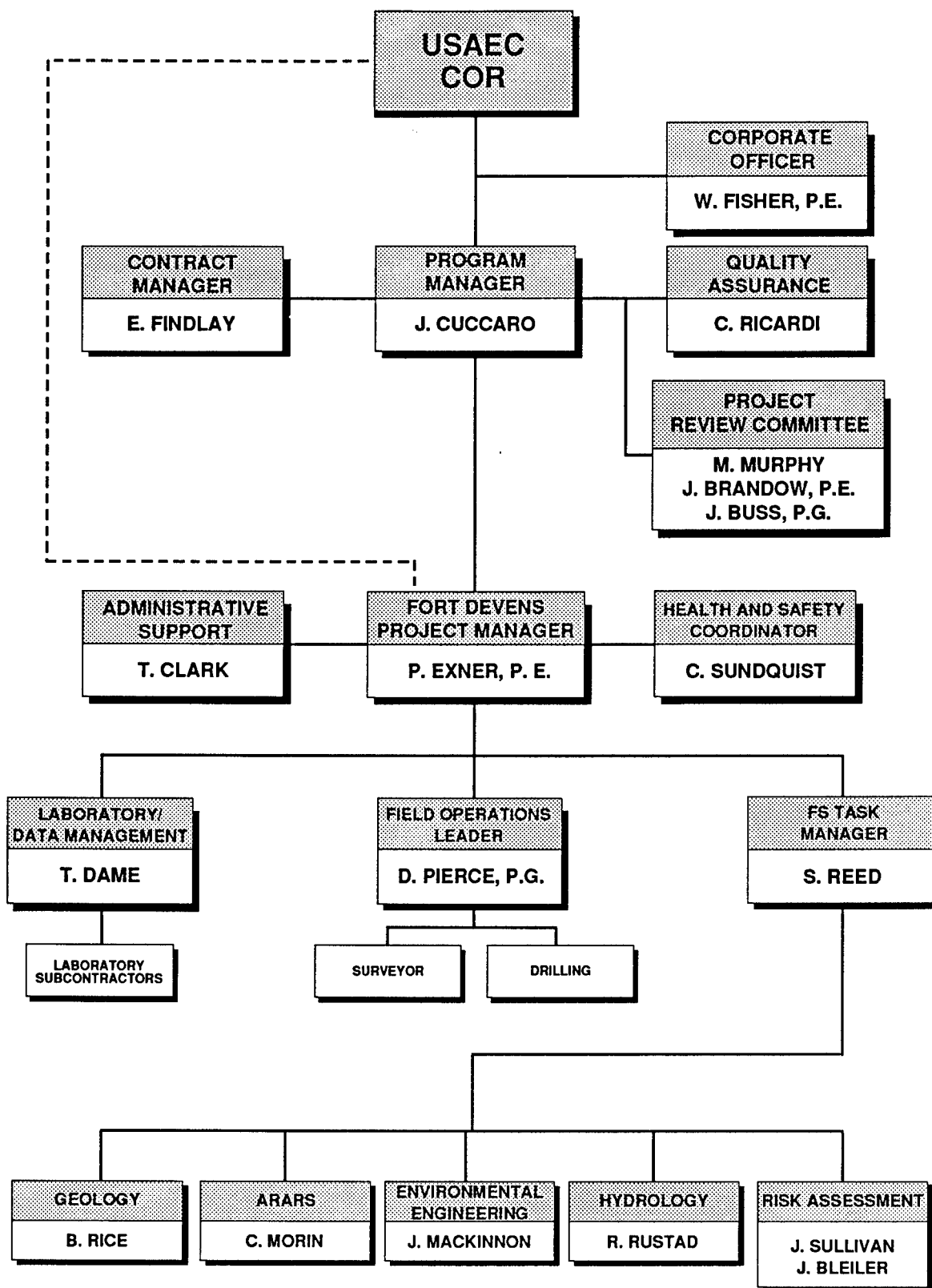


FIGURE 4
PROJECT ORGANIZATION
PLOW SHOP POND SUPPLEMENTAL INVESTIGATION
FEASIBILITY STUDY FOR GROUP 1A SITES
FORT DEVENS, MA

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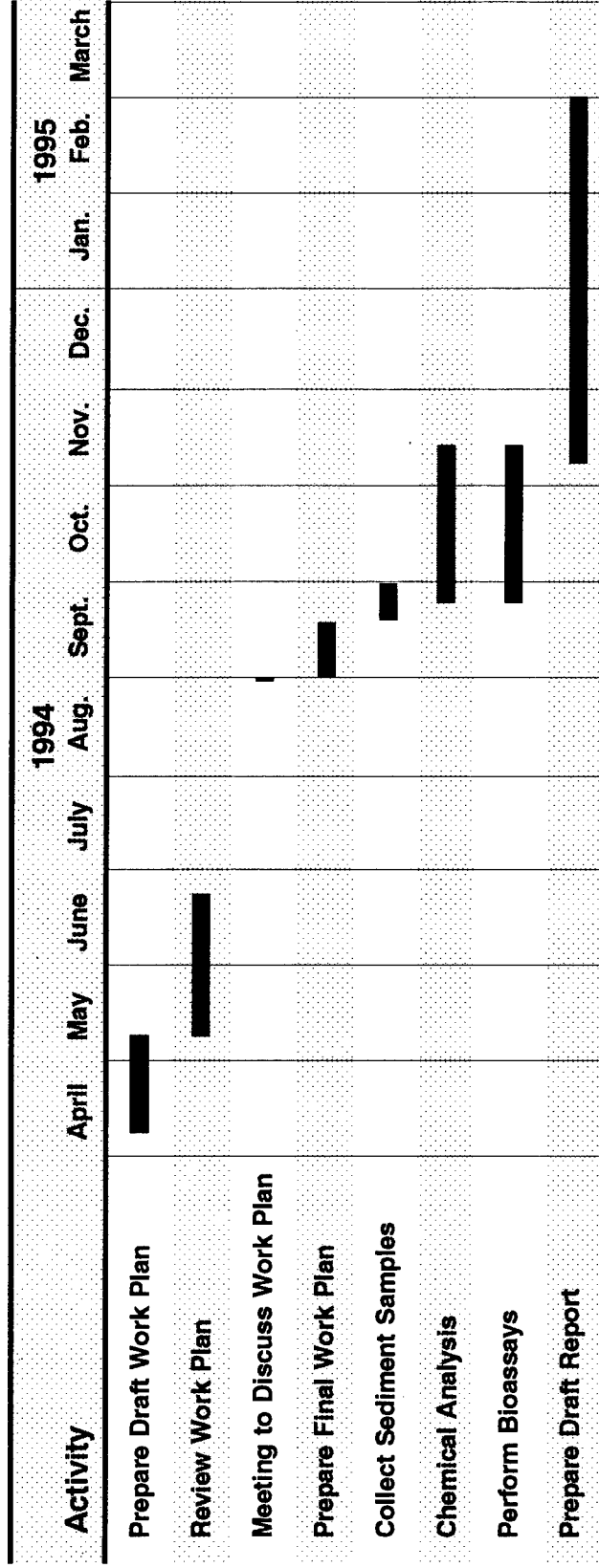


FIGURE 5
ACTIVITY SCHEDULE
PLOW SHOP POND SUPPLEMENTAL INVESTIGATION
FEASIBILITY STUDY FOR GROUP 1A SITES
FORT DEVENS, MA

TABLE 1
SUMMARY OF PROPOSED SUPPLEMENTAL INVESTIGATION ACTIVITIES

**PLOW SHOP POND SUPPLEMENTAL INVESTIGATION
FEASIBILITY STUDY FOR GROUP 1A SITES
FORT DEVENS, MA**

ACTIVITY	STATIONS	TEST MEDIUM	ANALYSES	PURPOSE
Sediment Evaluation	22 of 22	Bulk sediment	Total arsenic, barium, cadmium, cobalt, iron, manganese, nickel, chromium, copper, lead, zinc, and mercury. TOC, Simultaneously Extractable Metals (SEM), Acid Volatile Sulfides (AVS), and percent solids.	Better understand the relationships between bulk sediment chemistry, pore water concentrations, and bioavailability of inorganics.
Sediment Evaluation	10 of 22	Pore water (or elutriate)	Total arsenic, barium, cadmium, cobalt, iron, manganese, nickel, chromium, copper, lead, zinc, and mercury.	Better understand the relationships between bulk sediment and pore water concentrations.
Sediment Evaluation	10 of 22	Pore water (or elutriate) and bulk sediment	Methylmercury and total mercury.	Better understand the dynamics of mercury in sediment.
Toxicity Testing	22 of 22	Bulk sediment	Phase I sub-chronic <i>Ceriodaphnia dubia</i> and <i>Chironomus tentans</i> assays. <i>Hyallella azteca</i> to be evaluated at 10 of 22 stations.	Provide screening level toxicity testing of Plow Shop Pond sediment.
Toxicity Testing	3-5 of 22	Bulk sediment	Phase II dilution series sub-chronic <i>Ceriodaphnia dubia</i> and <i>Chironomus tentans</i> assays.	Assist with the development of PRGs.
Toxicity Testing	3-4 of 22	Pore water (or elutriate)	Phase III Toxicity Identification Evaluation.	Identify the toxicants responsible for any observed toxicity in laboratory bioassays.
Toxicity Testing	3-4 of 22	Bulk sediment	Phase IV Spiked Sediment Bioassays.	Provide a confirmation of the toxicants and the concentrations at which effects occur; assist with the development of PRGs.
Macroinvertebrate Study	NA	Benthic macro-invertebrates	Evaluate mouthpart deformities in archived chironomid midge larvae collected in the RI phase of work.	Provide "weight of evidence" information regarding impacts to the macroinvertebrate community.

continued

TABLE 1
SUMMARY OF PROPOSED SUPPLEMENTAL INVESTIGATION ACTIVITIES

PLOW SHOP POND SUPPLEMENTAL INVESTIGATION
FEASIBILITY STUDY FOR GROUP 1A SITES
FORT DEVENS, MA

ACTIVITY	STATIONS	TEST MEDIUM	ANALYSES	PURPOSE
Macroinvertebrate Study	5 of 22	Benthic macroinvertebrates	Evaluate mercury and methylmercury tissue burden in benthic macroinvertebrates.	Better understand the food chain distribution of mercury.
Human Health Study	NA	NA	Review literature relating sediment mercury contamination to fish tissue burden; review local consumption of fish and efficacy of fish consumption ban.	Assist with risk management activities and with the development of PRGs.

PRGs = Preliminary Remediation Goals

TABLE 2
SAMPLING AND LABORATORY ANALYSIS SCHEDULE
PLOW SHOP POND SUPPLEMENTAL INVESTIGATION
FEASIBILITY STUDY FOR GROUP 1A SITES
FORT DEVENS, MA

FILE TYPE	SITE TYPE	MEDIA	SITE ID	SAMPLE ID	MS/MSD	DUP	INORGANICS		METH. MERCURY		AVS	SEM	TOC	% SOLIDS
							SED	ELUT.	SED	ELUT.				
CSE	POND	Sediment	SHD-94-01X	DXSH0100			1	1	1	1	1	1	1	1
CSE	POND	Sediment	SHD-94-02X	DXSH0200			1				1	1	1	1
CSE	POND	Sediment	SHD-94-03X	DXSH0300			1				1	1	1	1
CSE	POND	Sediment	SHD-94-04X	DXSH0400			1				1	1	1	1
CSE	POND	Sediment	SHD-94-05X	DXSH0500			1				1	1	1	1
CSE	POND	Sediment	SHD-94-06X	DXSH0600			1				1	1	1	1
CSE	POND	Sediment	SHD-94-07X	DXSH0700			1	1	1	1	1	1	1	1
CSE	POND	Sediment	SHD-94-08X	DXSH0800			1	1	1	1	1	1	1	1
CSE	POND	Sediment	SHD-94-09X	DXSH0900			1	1	1	1	1	1	1	1
CSE	POND	Sediment	SHD-94-10X	DXSH1000		X	1	1	1	1	1	1	1	1
CSE	POND	Sediment	SHD-94-11X	DXSH1100			1				1	1	1	1
CSE	POND	Sediment	SHD-94-12X	DXSH1200	X		1	1	1	1	1	1	1	1
CSE	POND	Sediment	SHD-94-13X	DXSH1300			1	1	1	1	1	1	1	1
CSE	POND	Sediment	SHD-94-14X	DXSH1400			1	1	1	1	1	1	1	1
CSE	POND	Sediment	SHD-94-15X	DXSH1500			1				1	1	1	1
CSE	POND	Sediment	SHD-94-16X	DXSH1600			1	1	1	1	1	1	1	1
CSE	POND	Sediment	SHD-94-17X	DXSH1700			1				1	1	1	1
CSE	POND	Sediment	SHD-94-18X	DXSH1800			1				1	1	1	1
CSE	POND	Sediment	SHD-94-19X	DXSH1900			1	1	1	1	1	1	1	1
CSE	POND	Sediment	SHD-94-20X	DXSH2000			1				1	1	1	1
CSE	POND	Sediment	SHD-94-21X	DXSH2100			1				1	1	1	1
CSE	POND	Sediment	SHD-94-22X	DXSH2200			1				1	1	1	1
CHEMICAL SAMPLE SUBTOTAL							22	10	10	10	22	22	22	22
Trip Blanks							0	0	0	0	0	0	0	0
Duplicates @ 5%							1	1	1	1	1	1	1	0
MS/MSD Samples @ 5%							1	1	0	0	0	1	1	0
Rinsate Blanks @ 5%							1	0	0	0	0	0	0	0
CHEMICAL SAMPLE TOTAL							25	12	11	11	23	24	24	22

NOTES:
1. Inorganics include arsenic, barium, cadmium, chromium, cobalt, copper, iron, lead, manganese, mercury, nickel, and zinc.
2. MS/MSD = Matrix spike/Matrix spike duplicate

**USEPA DRAFT ANALYTICAL METHOD FOR DETERMINATION OF
ACID VOLATILE SULFIDE IN SEDIMENT**

ABB Environmental Services, Inc.



United States
Environmental Protection Agency
Office of Water

Office of Science and Technology
Health and Ecological Criteria Div.
Washington, DC 20460

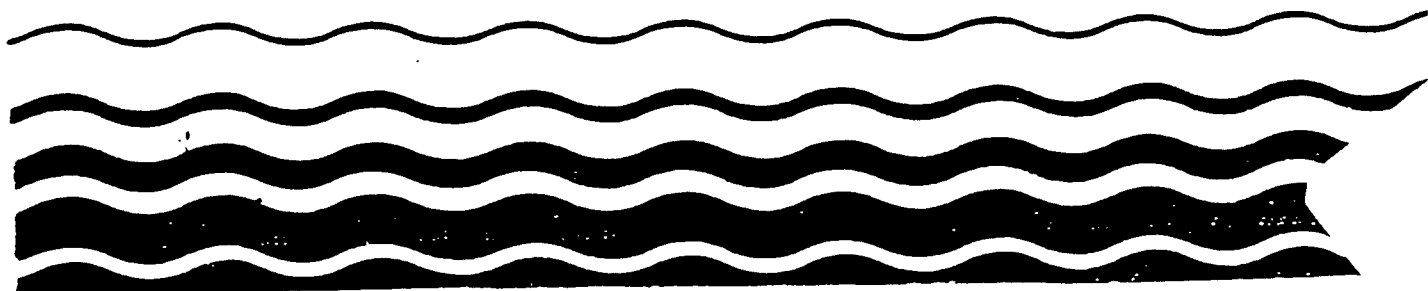
EPA xxx/x-xx-xxx

WATER

Draft Analytical Method

for Determination of Acid

Volatile Sulfide in Sediment



**DETERMINATION OF ACID VOLATILE SULFIDE AND
SELECTED SIMULTANEOUSLY EXTRACTABLE METALS IN
SEDIMENT**

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DETERMINATION OF ACID VOLATILE SULFIDE AND SELECTED SIMULTANEOUSLY EXTRACTABLE METALS IN SEDIMENT

1. SCOPE AND APPLICATION

- 1.1 This method describes procedures for the determination of acid volatile sulfide (AVS) and for selected metals that are solubilized during the acidification step (simultaneously extracted metal, SEM). As a precipitant of toxic heavy metals, sulfide is important in controlling the bioavailability of metals in anoxic sediments (1). Research has established that the relative amounts of SEM and AVS are important in the prediction of potential metal bioavailability; if the molar ratio of SEM for bivalent metals to AVS exceeds one, the toxic heavy metals in that sample are potentially bioavailable. This method uses the same conditions for release of both sulfide and metal from the sediment and thus provides a useful means of assessing the amount of metal associated with sulfide.

2. SUMMARY OF METHOD

- 2.1 The AVS in the sample is first converted to hydrogen sulfide (H_2S) by acidification with hydrochloric acid at room temperature. The H_2S is then purged from the sample and trapped in aqueous solution. The amount of sulfide that has been trapped is then determined. The SEM are selected metals liberated from the sediment during the acidification. These are determined after filtration of the sample.
- 2.2 Two types of apparatus for sample purging and trapping of H_2S are described. One uses a series of Erlenmeyer flasks while the other uses flasks and traps with ground glass stoppers. The former is less costly. The latter is less prone to leakage that causes low recovery of AVS. The latter is recommended when higher degrees of precision are desired and for samples containing low levels of AVS.
- 2.3 Three means of quantifying the H_2S released by acidifying the sample are provided. The colorimetric method is generally preferred. In the gravimetric procedure, the H_2S is trapped in silver nitrate. The silver sulfide that is formed is determined by weighing (1, 2). This procedure can be used for samples with moderate or high AVS concentrations. Below 10 μ moles AVS/gram dry sediment, accuracy may be affected by incomplete recovery of precipitate and by weighing errors. In the colorimetric method, the H_2S is trapped in sodium hydroxide. The sulfide reacts with N-N-dimethyl-p-phenylenediamine to form methylene blue that is measured (3). This procedure is capable of determining AVS concentrations as low as 0.01 μ moles/gram dry weight of sediment. By appropriate sample dilution, the maximum concentration of

AVS which can be determined is at least 1000 μ moles/gram dry sediment. In an alternative procedure the H_2S is trapped in an antioxidant buffer before using an ion-selective electrode (4, 5).

- 2.4 After release of the H_2S , the acidified sediment sample is membrane filtered before determination of the SEM by atomic absorption or inductive coupled plasma spectrometric methods (6, 7).

3. DEFINITIONS

- 3.1 **ACID VOLATILE SULFIDE (AVS)** - AVS is operationally defined as sulfides that form hydrogen sulfide under the conditions of this test. This includes amorphous, moderately crystalline monosulfides, and other sulfides (8).
- 3.2 **SIMULTANEOUSLY EXTRACTED METALS (SEM)** - SEM are operationally defined as metals, commonly cadmium, copper, lead, mercury, nickel and zinc, that form less soluble sulfides than do iron or manganese, and which are at least partially soluble under the conditions of this test.
- 3.3 **METHOD DETECTION LIMIT (MDL)** - The minimum concentration of an analyte that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. The MDL is determined from the analysis of a sample that contains the analyte within a given matrix.
- 3.4 **LABORATORY REAGENT BLANK (LRB)** - An aliquot of reagent water or reagents that is treated exactly as a sample including exposure to all glassware, equipment, and reagents that are used with samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, reagents or apparatus.
- 3.5 **STOCK STANDARD SOLUTION** - A concentrated solution of the analyte prepared in the laboratory using assayed reference compounds or purchased from a reputable commercial source.
- 3.6 **CALIBRATION STANDARDS** - Solutions prepared from the stock standard solution that is used to calibrate the method response with respect to analyte concentration.
- 3.7 **LABORATORY FORTIFIED BLANK (LFB)** - An aliquot of reagent water or reagents to which a known quantity of the method analyte is added in the laboratory. The LFB is analyzed exactly like a sample. Its purpose is to determine whether the method is within accepted control limits.
- 3.8 **LABORATORY FORTIFIED SAMPLE MATRIX (LFM)** - An environmental sample to which a known quantity of the method analyte is added in the laboratory. The LFM is

analyzed exactly like a sample. Its purpose is to determine whether the sample matrix contributes bias to the analytical results.

4. INTERFERENCES

- 4.1 Contact with oxygen must be avoided in all stages from sampling to analysis. Consequently, the samples and standards should be protected from air from the time of sampling through the analytical procedure. This can be achieved by deaerating and maintaining the samples under nitrogen or argon at all times.

5. SAFETY

- 5.1 The toxicity or carcinogenicity of reagents used in this method have not been fully established. Each chemical and environmental sample should be regarded as a potential health hazard and exposure should be minimized. Each laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets should be available to all personnel involved in the chemical analysis.
- 5.2 Hydrogen sulfide is a highly poisonous, gaseous compound having a characteristic odor of rotten eggs. It is detectable in air by humans at a concentration of approximately 0.002 ppm. Handling of acid samples should be performed in a hood or well ventilated area. If a high concentration of hydrogen sulfide is detected in the air by the laboratory staff, sample handling procedures must be corrected. According to Sax (9) an air concentration of 10 ppm of H_2S is permitted for an 8 hour shift for 40 hours per week.
- 5.3 If samples originate from a highly contaminated area, appropriate sample handling procedures to minimize worker exposure must be followed.

6. APPARATUS AND EQUIPMENT

6.1 Glassware

6.1.1 AVS evolution and H_2S trapping - Glassware in Section 6.1.1.1 is recommended. Glassware in Section 6.1.1.2 may be used, but will not provide as high precision or accuracy for samples.

6.1.1.1 For highest precision and low AVS levels - For each analytical train 500 mL gas washing bottles or oxygen trap, one 250 mL round bottom flask with a septum (Ace Glass 6934 or equivalent), 100 or

250 mL impingers with non-fritted outlets. The round bottom flask contains the sediment and acid is introduced to it by a syringe inserted through the septum. The flasks are connected by tubing. Because sulfide may react with tubing and other surfaces, minimum lengths of tubing should be used as sleeves to connect the glass tubing. The analyst should pay particular attention to the recovery of sulfide from standards in evaluating the apparatus. In all cases the inlets are below the liquid level and the outlets are above the liquid levels. The apparatus is assembled as shown in Figure 1 and more than one analytical train can be connected to a single cylinder of nitrogen or argon if flow controllers are installed in the line. Different amounts of glassware are required for each of the three means of sulfide determination.

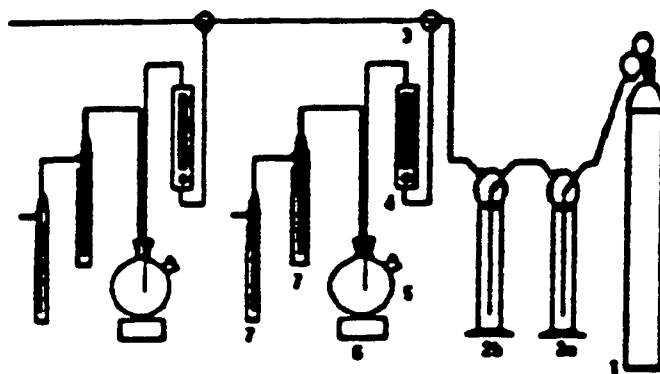


Figure 1. Apparatus for AVS determination: 1. N_2 or Ar cylinder; 2. Gas washing bottles: (a) oxygen scrubbing solution or an oxygen trap may be used in replacement of this gas washing bottle, (b) deionized water; 3. Three-way stopcock; 4. Flow controller; 5. Reaction flask; 6. Magnetic stirrer; 7. Impingers with non-fritted outlets.

6.1.1.2 For routine analysis - Erlenmeyer flasks, 250 mL, are substituted for the gas washing bottle, the round bottom flask and the impingers. The flask size should be consistent with sample size and reagent volumes. A thistle tube fitted with a stopcock or a separatory funnel is provided to introduce acid to the flask containing the sediment sample. This flask is fitted with a three hole stopper. One hole is for the thistle tube or separatory funnel and the other two are for the gas inlet and

outlet. The other flasks are fitted with two hole stoppers; one hole is for the gas inlet and the other is for the gas outlet. The gas inlets are below the liquid level and the gas outlets are above the liquid level. The flasks are connected by tubing. Because sulfide may react with tubing, stoppers and other surfaces, minimum lengths of tubing should be used as sleeves to connect the glass tubing. The analyst should pay particular attention to the recovery of sulfide from standards in evaluating the apparatus.

- 6.1.2 Evaporating dishes, porcelain, 100 mL.
- 6.1.3 Assorted calibrated pipettes and volumetric flasks.
- 6.2 Drying oven - Capable of maintaining a constant temperature in the range of 103-105°C.
- 6.3 Analytical balance - capable of weighing to 0.0001 g.
- 6.4 Magnetic stirrer, thermally insulated, and Teflon-coated stirring bar.
- 6.5 Gravimetric method
 - 6.5.1 Filtering flask.
 - 6.5.2 Filter holder for 47 mm filter.
- 6.6 Colorimetric method
 - 6.6.1 Spectrophotometer - Capable of measuring absorbance at 670 nm.
 - 6.6.2 Spectrophotometer cells.
- 6.7 Ion-selective electrode method
 - 6.7.1 Electrometer, pH meter or ion-selective meter - Compatible with the use of ion-selective electrodes.
 - 6.7.2 Sulfide selective electrode.
 - 6.7.3 Double-junction reference electrode.
- 6.8 Atomic absorption or inductive couple plasma spectrophotometer for the determination of SEM.

7. REAGENTS AND CONSUMABLE MATERIALS

- 7.1 All water and reagents used in this method must be free of dissolved oxygen and sulfide. Freshly prepare and use deaerated, deionized water by removing dissolved

oxygen from the deionized water by vigorously bubbling with oxygen-free nitrogen or argon for approximately one hour. Deaerate reagents immediately before use by deaerating with oxygen-free nitrogen or argon.

7.2 Sodium sulfide standard - Required for quality assurance and calibration.

7.2.1 Sulfide stock standard solution, approximately 0.05M or 50 $\mu\text{moles/mL}$.

7.2.1.1 Weigh about 12 gram of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ and dissolve it in 1,000 mL of deionized water. Store in a brown bottle. To prevent air oxidation, the sulfide solution should be maintained under oxygen-free nitrogen or argon.

7.2.1.2 Standardize against thiosulfate solution.

7.2.1.2.1 Pipette 10.00 mL of 0.025N standard iodine solution (Section 7.2.2) into each of two 125-mL Erlenmeyer flasks.

7.2.1.2.2 Pipette 2.00 mL of sulfide stock standard solution into one flask. Pipette 2.00 mL of deionized water, as a laboratory reagent blank, into the other flask.

7.2.1.2.3 Add 5.00 mL of 6M HCl into each flask, swirl slightly, then cover and place in the dark for 5 minutes.

7.2.1.2.4 Titrate each with 0.025N thiosulfate (Section 7.2.3) until the yellow iodine color fades to a pale straw. Just before all the iodine has been titrated, add starch indicator (Section 7.2.4) dropwise to form a pale blue color. Continue the titration with the thiosulfate. The end point is reached when the blue color first disappears.

7.2.1.2.5 Calculate the sulfide concentration as follows:

$$\text{Sulfide } (\mu\text{mol/mL}) = \frac{(T_{\text{blank}} - T_{\text{sample}}) \times N_{\text{S}_2\text{O}_3^{2-}}}{V_{\text{sample}}} \times \frac{1 \text{ mole S}^{2-}}{2 \text{ equiv S}^{2-}} \times \frac{1000 \mu\text{moles}}{1 \text{ mmole}}$$

where T = volume of titrant used for the blank and sample (mL)

N = concentration of $\text{S}_2\text{O}_3^{2-}$ titrant

V = volume of sample used (mL), 2.00 mL recommended

7.2.2 Standard iodine solution, 0.025N - Dissolve 20 to 25 gram potassium iodide, KI, in a small volume of deionized water, add 3.2 gram iodine, and dilute to 1,000 mL. Standardize against 0.025N sodium thiosulfate (Section 7.2.3)

7.2.3 Standard sodium thiosulfate solution, 0.025N. May be purchased commercially or prepared in the laboratory. Standardize against potassium bi-iodate.

7.2.3.1 Weigh approximately 6.2 g of sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{H}_2\text{O}$, into a 500 mL beaker. Add 0.1 g sodium carbonate, Na_2CO_3 , and dissolve in 400 mL deionized water. Pour into a 1.0 L volumetric flask and dilute to volume with deionized water.

7.2.3.2 Standardization against potassium bi-iodate, $\text{KH}(\text{IO}_3)_2$.

7.2.3.2.1 Prepare 0.00208M potassium bi-iodate by dissolving 0.8123 g $\text{KH}(\text{IO}_3)_2$, previously dried 2 hr at 103-105°C, in distilled water. Pour into a 1.0 L volumetric flask and dilute to volume with deionized water.

7.2.3.2.2 Dissolve approximately 2 g KI, free from iodate, in an erlenmeyer flask with 100 to 150 mL deionized water. Add 1 mL of 6N H_2SO_4 or a few drops of concentrated H_2SO_4 and 20.00 mL of standard bi-iodate solution. Dilute to 200 mL and titrate the liberated iodine with the thiosulfate solution until the yellow color fades to a pale straw color. Then add a couple drops of starch indicator to form a pale blue color and continue the titration with the thiosulfate until the blue color first disappears.

7.2.3.2.3 20.00 mL of 0.00208M $\text{KH}(\text{IO}_3)_2$ requires exactly 20.00 mL of 0.025N sodium thiosulfate. For an calculation of the thiosulfate concentration use the following equation:

$$N(\text{S}_2\text{O}_3^{2-}) = \frac{\text{g KH}(\text{IO}_3)_2}{\text{mL S}_2\text{O}_3^{2-}} \times \frac{1 \text{ mole KH}(\text{IO}_3)_2}{389.9 \text{ g KH}(\text{IO}_3)_2} \times \frac{12 \text{ equiv KH}(\text{IO}_3)_2}{1 \text{ mole KH}(\text{IO}_3)_2} \times \frac{1000 \text{ mL}}{1 \text{ L}}$$

7.2.4 Starch indicator - Dissolve 1.0 gram soluble starch in 100 mL boiling deionized water.

7.2.5 Sulfide working standards - Prepare sulfide working standards using the sulfide stock standard solution in Section 7.2.1. The concentrations of the following standards will depend on the exact concentration of the sulfide stock standard determined in Section 7.2.1.2.5. Correct concentrations of the standards in the following part of this section and the amount of sulfide in standards used in the colorimetric method in Section 12.2.5 by multiplying by a factor of the concentration determined in Section 7.2.1.2.5 divided by 50 $\mu\text{moles/mL}$.

7.2.5.1 Prepare sulfide working standard A by diluting 1.00 mL of sulfide stock standard to 100.0 mL. This solution contains 0.5 μ mole sulfide/mL, if the concentration of the sulfide stock standard is exactly 0.05M.

7.2.5.2 Prepare sulfide working standard B by diluting 10.00 mL of sulfide stock standard to 100.0 mL. This solution contains 5.0 μ mole sulfide/mL, if the concentration of the sulfide stock standard is exactly 0.05M.

7.3 AVS evolution

7.3.1 Hydrochloric acid 6M - Dilute 500 mL of concentrated hydrochloric acid (sp. gr. 1.19) to 1L with deionized water. Deaeration of this solution as described in Sections 7.1 and 11.4 is most important.

7.3.2 Nitrogen or argon gas, oxygen free, with regulator and flow controller. An oxygen gas scrubber may be required and is available commercially or deoxygenating solutions may be placed in the first flask or gas washing bottle in the analytical train.

7.3.3 Plastic hypodermic syringe, 30 mL, and needle.

7.4 Gravimetric method

7.4.1 Potassium acid phthalate, 0.05M - Dissolve 10.2 g of potassium acid phthalate, $\text{KHC}_8\text{H}_4\text{O}_4$, in deionized water and dilute to 1L.

7.4.2 Silver nitrate, 0.1M - Dissolve 17 g of silver nitrate, AgNO_3 , in deionized water and dilute to 1L. Store in a dark bottle.

7.4.3 Glass fiber filters, 1.2 micron - Rinse with deionized water, then predry filters at 103-105°C.

7.5 Colorimetric method

7.5.1 Sodium hydroxide solution, 1M - Dissolve 40 g sodium hydroxide in 1000 mL deionized water.

7.5.2 Sodium hydroxide solution, 0.5M - Dissolve 20 g sodium hydroxide in 1000 mL deionized water.

7.5.3 Mixed diamine reagent, MDR

7.5.3.1 Component A - Add 660 mL concentrated sulfuric acid to 340 mL of deionized water. After the solution cools, dissolve 2.25 g N-N-dimethyl-p-phenylenediamine oxalate in it.

7.5.3.2 Component B - Dissolve 5.4 g ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) in 100 mL concentrated hydrochloric acid and dilute to 200 mL with deionized water.

7.5.3.3 Mixed diamine reagent, MDR - Mix components A and B.

7.5.4 Sulfuric acid solution, 1.0M - Dilute 56 mL concentrated sulfuric acid (H_2SO_4) to 1 L with deionized water.

7.6 Ion-selective electrode method

7.6.1 Sodium hydroxide solution - Dissolve 80 g of sodium hydroxide in 700 mL of deionized water with caution. Cool to room temperature.

7.6.2 Sulfide anti-oxidant buffer (SAOB) - To the sodium hydroxide solution in Section 7.6.1 add and dissolve 74.45 g of disodium ethylenediaminetetraacetic acid and 35.23 g of ascorbic acid. Dilute to 1L with deionized water.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 Sulfide ion is unstable in the presence of oxygen. Protect sediment samples from exposure to oxygen during sample collection and storage.

8.2 During storage sulfide can be formed or lost due to biological activity and sulfide can be lost by volatilization or oxidation. Metal speciation can change as a result of changes in sulfide concentration and as a result of other changes in the sample.

8.3 Samples should be collected in wide mouth jars with a minimum of air space above the sediment. If possible, the headspace should be filled with oxygen free nitrogen or argon. The jar lids must have Teflon or polyethylene liners.

8.4 Samples should be cooled to 4°C as soon as possible after collection. Samples maintained at 4°C have been found to have no significant loss of AVS for storage periods up to 2 weeks (3). Holding time for samples should not exceed 14 days.

9. CALIBRATION AND STANDARDIZATION

9.1 Calibrate the photometer with a minimum of four standards and a blank that cover the expected range of the samples. Prepare a calibration graph relating absorbance to the μmoles of sulfide taken.

9.2 Calibrate the sulfide electrode system with a minimum of three standards that cover the expected range of the samples. Standards must be made up in SAOB diluted 1+1 with deionized water. Follow the manufacturer's instructions for use of the electrode.

- 9.3 Overall sulfide recovery is determined by analysis of a known amount of sodium sulfide standard added to deionized water from which the sulfide is liberated in the analysis train (LFB). Recoveries of $95\% \pm 10\%$ are expected.

10. QUALITY CONTROL

- 10.1 Each laboratory using this method is required to operate a formal quality control (QC) program. The minimum requirement of this program consists of an initial demonstration of laboratory capability, and the analysis of laboratory reagent blanks, fortified blanks and fortified samples as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of data thus generated.

10.2 INITIAL DEMONSTRATION OF PERFORMANCE

- 10.2.1 The initial demonstration of performance is used to characterize instrument performance, method detection limits, and linear calibration ranges.
- 10.2.2 Method detection limit (MDL) - The method detection limit should be established for the analyte, using deionized water (blank) fortified at a concentration two to five times the estimated detection limit (10). To determine MDL values, take seven replicate aliquots of the fortified reagent water and process through the entire analytical method. Perform all calculations and report the concentration values in the appropriate units. Calculate the MDL as follows:

$$MDL = t \times s$$

where, t = students' t value for a 99% confidence level and a standard deviation estimate with $n-1$ degrees of freedom ($t = 3.14$ for seven replicates), and
 s = standard deviation of the replicate analyses.

Method detection limits should be determined every six months or whenever a significant change in background or instrument response is expected.

- 10.2.3 Linear calibration ranges - The upper limit of the linear calibration range should be established by determining the signal responses from a minimum of four different concentration standards covering the expected range, one of which is close to the upper limit. The linear calibration range that may be used for the analysis of samples should be judged by the analyst from resulting data. Linear calibration ranges should be determined every six months or whenever a significant change in instrument response may be expected.

10.3 ASSESSING LABORATORY PERFORMANCE - REAGENT AND FORTIFIED BLANKS

- 10.3.1 Laboratory reagent blank (LRB) - The laboratory must analyze at least one laboratory reagent blank (Section 3.4) with each set of samples. Reagent blank data are used to assess contamination from the laboratory environment and reagents. If an analyte value in the reagent blank exceeds its determined MDL, then laboratory or reagent contamination should be suspected. Any determined source of contamination should be corrected and the samples reanalyzed.
- 10.3.2 Laboratory fortified blank (LFB) - The laboratory must analyze at least one laboratory fortified blank (Section 3.7) with each set of 20 samples. Calculate accuracy as percent recovery. If the recovery of the analyte falls outside the control limits (Section 10.3.3), the analyte is judged to be out of control, and the source of the problem should be identified and resolved before continuing analyses.
- 10.3.3 Until sufficient data become available from within their own laboratory (usually a minimum of twenty to thirty analyses), the laboratory should assess laboratory performance against recovery limits of 85-105%. When sufficient internal performance data becomes available, develop control limits from the mean recovery (\bar{x}) and the standard deviation (s) of the mean recovery. These data are used to establish upper and lower control limits as follows:

$$\text{UPPER CONTROL LIMIT} = \bar{x} + 3s$$

$$\text{LOWER CONTROL LIMIT} = \bar{x} - 3s$$

After each five to ten new recovery measurements, new control limits should be calculated using only the most recent twenty to thirty data points.

10.4 ASSESSING ANALYTE RECOVERY - LABORATORY FORTIFIED SAMPLE MATRIX

- 10.4.1 The laboratory must fortify a minimum of 10% of the routine samples or one fortified sample per set of 20 samples, whichever is greater. At least one sample from each source should be fortified. Ideally, the concentration should at least double the background concentration. Over time, samples from all routine sample sources should be fortified.
- 10.4.2 Calculate the percent recovery for the analyte, corrected for background concentrations measured in the unfortified sample, and compare these values to the control limits established in Section 10.3.3 for the analyses of LFBs. Spike recovery calculations are not required if the spike concentration is less than 10%

of the sample background concentration. Percent recovery may be calculated in units appropriate to the matrix, using the following equation:

$$R = \frac{(C_s - C_b)}{S} \times 100$$

where

R = percent recovery,

C_s = fortified sample concentration,

C_b = sample background concentration, and

S = concentration equivalent of the fortified sample.

10.4.3 If the recovery of the analyte in the fortified sample falls outside the designated range, and the laboratory performance on the LFB for the analyte is shown to be in control (Section 10.3) the recovery problem encountered with the fortified sample is judged to be matrix related, not system related.

11. GENERATION OF H₂S

11.1 Assemble glassware according to the detection method to be used. The setup in Figure 1 should be followed as a general guide. In all cases a flask or gas washing bottle containing a deoxygenating solution may be placed in the sample train between the nitrogen or argon tank and the first flask. Glassware is specified in Section 6.1.1. It is recommended that nitrogen or argon be controlled by a flow controller, but an equivalent flow rate may be regulated by a clamp and bubble rate determined. In all cases the glassware will minimally consist of a H₂S generating flask and a series of traps.

11.1.1 Gravimetric method - The first flask contains the sediment sample or standard. The second flask contains 175-200 mL of potassium hydrogen phthalate reagent 7.4.1 as an HCl trap. The third and fourth flasks contain 175-200 mL of silver nitrate reagent 7.4.2. If glassware specified in Section 6.1.1.1 is used, the second flask is a gas washing bottle and the third and fourth flasks are impingers.

11.1.2 Colorimetric method - The first flask contains the sediment sample or standard. The second and third flask contain an absorbant of 80 mL 0.5M NaOH reagent 7.5.2. If glassware specified in Section 6.1.1.1 is used, the second and third flasks are impingers.

- 11.1.3 Ion-selective electrode method - The first flask contains the sediment sample or standard. The second and third flask contain an absorbant of 50 mL SAOB reagent 7.6.2 and 30 mL deionized water. If glassware specified in Section 6.1.1.1 is used, the second and third flasks are impingers.
- 11.2 One hundred milliliters (100 mL) of deionized water and a magnetic stirring bar are added to the flask that will contain the sediment. The total volume of deionized water plus water contained in the wet sediment sample should not exceed 120 mL to minimize differences in acid concentration among samples. For the computation of the volume of water contained in the wet sediment, see Section 13.3. The traps are filled and deaerated by bubbling nitrogen or argon for 10 minutes at a flowrate of 100 cm³/min. Reduce flow to 40 cm³/min.
- 11.3 Weigh approximately 10 g of wet sediment on an analytical balance. Record weight to the nearest milligram. If AVS concentration is high, a smaller amount of sediment may be required; use of sediment samples smaller than 1-2 grams is not recommended due to sulfide oxidation and sample heterogeneity. Use of large sediment samples is not recommended because significant amounts of acid may be neutralized. Place sediment in the standard taper round bottom flask or the Erlenmeyer flask fitted with the thistle tube or separatory funnel. Parafilm has been found to be free of sulfide (4). Weigh samples on 2 × 2 inch pieces of parafilm and introduce the parafilm and sample to the flask. Rinsing the sample into the flask is not recommended. Purge the sample for 10 minutes with nitrogen or argon at a flowrate of 40 cm³/min. Stop the flow of gas.
- 11.4 Using a 30 mL syringe, inject 20 mL of 6M HCl, which has been bubbled with nitrogen or argon gas for 30 minutes, into the reactor through the septum. If the apparatus described in Section 6.1.1.1 is used, add the HCl from the thistle tube or the separatory funnel. Bubble nitrogen or argon through the sample for 1 hour at a flowrate of 20 cm³/min and magnetically stir the sample at the same time.
- 11.5 Analyze sulfide contained in sulfide trap by the appropriate analytical procedure in Section 12.

12. ANALYSIS OF SULFIDE

12.1 Gravimetric method

12.1.1 Insure that the final trap, the second silver nitrate trap, contains no precipitate.

12.1.2 Filter the silver sulfide contained in the first sulfide trap through a preweighed 1.2 micron filter. Rinse filter with deionized water. Dry at 103-105°C and weigh.

12.1.3 Calculate the amount of silver sulfide as the difference between the weight of silver sulfide and the filter and the weight of the predried filter.

12.1.4 Calculate the amount of sulfide in the sample:

$$\text{Sulfide in wet sediment } (\mu\text{moles}) = \frac{\text{g Ag}_2\text{S}}{247.8} \times 10^6$$

12.2 Colorimetric method

12.2.1 If the AVS concentration is low so that the sulfide contained in the tube trap is less than 15 μmoles , add 10 mL of the mixed diamine reagent (MDR) directly to the NaOH solution in each trap tube to develop the color. Transfer this solution to a 100 mL volumetric flask and dilute to the mark with deionized water. If the sulfide contained in the NaOH in the tube trap exceeds 18 μmoles , transfer the NaOH in each tube trap to a 100 mL volumetric flask. Rinse the trap with deaerated 0.5M NaOH and dilute to volume with NaOH. An appropriate volume aliquot of this solution is used for the analysis. In this case, the aliquot is transferred to a 100 mL volumetric flask, sufficient 0.5M NaOH is added so that the total volume is 80 mL, 10 mL MDR is added, and the solution is diluted to 100 mL with deionized water. Use of sediment samples smaller than 1-2 grams is not recommended due to sulfide oxidation and sample heterogeneity.

12.2.2 After 30 minutes, but before two hours have elapsed, measure the absorbance of light at 670 nm using a half-inch diameter or 1 cm rectangular spectrophotometer cell.

12.2.3 If the absorbance of the sample is greater than 0.6, dilute 10-fold with 1.0M H_2SO_4 and compare to the high range calibration curve.

12.2.4 Normally, the sulfide concentration in second trap tube is close to the blank value in this procedure and is not significant in calculating the concentration of sulfide. If a significant color is developed, the flow rate and amount of sulfide in the standard or sediment should be checked

12.2.5 Preparation of calibration curve - The indicated amounts of sulfide are based on a 0.05M concentration of the sulfide stock standard solution. The procedure indicated in Section 7.2.5 should be used to calculate the exact amount of sulfide in each of the standards.

12.2.5.1 Low range calibration curve - 0.0 - 2.5 $\mu\text{moles S}^{2-}$ (0.0 - 80 $\mu\text{g S}^{2-}$)

Add 80 mL 0.5 N sodium hydroxide to each of a series of 100 mL of flasks and add 0.00, 1.00, 2.00, 3.00, 4.00, and 5.00 mL of sulfide working standard A to these flasks. These samples contain 0.00,

0.50, 1.00, 1.50, 2.00, and 2.50 $\mu\text{moles S}^{2-}$, respectively. Add 10.0 mL of MDR to each and dilute to 100.00 mL with deionized water. After 30 minutes, measure the absorbance at 670 nm.

12.2.5.2 High range calibration curve - 0.0 - 20.0 $\mu\text{moles S}^{2-}$
(0.0 - 640 $\mu\text{g S}^{2-}$)

Add 80 mL 0.5M sodium hydroxide in 100 mL flasks and add 0.00, 1.00, 2.00, 3.00 and 4.00 mL of sulfide working standard B to these flasks. These samples contain 0.0, 5.00, 10.00, 15.00, and 20.00 $\mu\text{moles S}^{2-}$, respectively. Add 10.0 mL of MDR and dilute to 100.00 mL with deionized water. After 30 minutes, dilute the solution 10-fold with 1.0M H_2SO_4 , and measure the absorbance at 670 nm.

12.2.6 Calculate the amount of sulfide (μmoles) in the sample from the calibration curve. If the total volume of NaOH in the trap was not used in the analysis, account for the portion tested.

12.3 Ion-selective electrode method

12.3.1 Calibrate the sulfide electrode and meter according to manufacturer's recommendations, using sulfide standards prepared in SAOB reagent 7.6.2 diluted 1:1 with deionized water.

12.3.2 Transfer the contents of each sulfide trap into a 100-mL volumetric flask. Rinse the trap with deionized water, adding the rinses to the volumetric flask. Dilute to volume with deionized water.

12.3.3 Pour contents of volumetric flask into a 150-mL beaker, add a stirring bar and place on stirrer. Begin stirring with minimum agitation to avoid entrainment of air into the solution and minimize oxidation of the sample during the measurement.

12.3.4 Rinse sulfide and reference electrodes into waste container and blot dry with absorbent tissue. Immerse electrodes in sample solution.

12.3.5 Allow electrode response to stabilize (8-10 minutes), then take measurement of sulfide concentration. Depending on the meter used, the reading may be directly in concentration units if the meter is in the concentration mode and a 2-point calibration has been performed. If the readings are in millivolts, convert millivolts to concentration using the calibration curve obtained from standard solutions.

12.3.6 Calculate the amount of sulfide (μmoles) in the sample.

13. CALCULATION OF AVS CONCENTRATION IN SEDIMENTS

- 13.1 The sediment dry weight/wet weight ratio (R) must be determined separately. Acid volatile sulfide can be oxidized or altered to non-volatile forms during drying.
- 13.2 Transfer an aliquot of the sediment to a tared 100-mL tared evaporating dish. Weigh the dish plus the wet sediment. Calculate the wet weight of the sample. Dry the sediment at 103-105°C and weigh. Calculate the dry weight of sediment.
- 13.3 Determine the ratio of dry weight to wet weight for the sediment sample:

$$R = \frac{W_d}{W_w}$$

where R = ratio of dry weight to wet weight,

W_d = dry weight of sediment sample (g), and

W_w = wet weight of sediment sample (g).

Also, the weight of water, W_{water} , taken in a sample for AVS analysis can be calculated. If the weight of the wet sediment sample taken for the AVS analysis is W_{s+w} , the weight of water contained in the sediment sample would be

$$W_{\text{water}} = W_{s+w} - (R \times W_{s+w})$$

The volume of water in the sample equals the weight of water, assuming the density is near unity.

- 13.4 Compute the sulfide concentration per gram dry weight of sediment:

$$\text{AVS } (\mu\text{moles/g}) = \frac{S}{R \times W_w}$$

where S = the amount of AVS in sediment (μmoles) from Section 12.1.4, 12.2.6, or 12.3.6, as appropriate,

R = ratio of dry weight to wet weight from Section 13.3, and

W_w = wet weight of sediment (g) taken for AVS analysis.

- 13.5 The QC data obtained during the analysis provides an indication of the quality of the sample data and should be provided with the sample results.

14. DETERMINATION OF SIMULTANEOUSLY EXTRACTED METALS (SEM)

- 14.1 After the generation of sulfide has been completed, filter the sediment suspension remaining in the H_2S generation flask (Section 11.4) through a 0.2 μ membrane filter

resistant to attack by acid. The filtering apparatus should be soaked in 0.1M HNO₃, then rinsed with deionized water prior to use.

14.2 Transfer the filtrate to a 250-mL volumetric flask. Rinse the filtering flask with distilled water, adding the rinses to the volumetric flask. Dilute to volume with deionized water. The volumetric flasks should be soaked in 0.1M HNO₃, then rinsed with deionized water prior to use. Samples should be analyzed within 2 weeks.

14.3 Determine the concentrations of sulfide binding metals of interest and those which, on a molar basis, are present at more than 1 percent of the AVS concentration. Do not include iron and manganese whose sulfides are less stable than are the sulfides of many trace metals. Metals which may typically be included in SEM are cadmium, copper, lead, mercury, nickel and zinc. In addition, antimony, bismuth and chromium, among others, form insoluble sulfides. If significant concentrations of these or other metals forming insoluble sulfides are present, their concentrations should be taken into account in the computation of SEM. However, if these or other metals which are not divalent are present in significant concentrations, the computation in Section 14.5 must be modified to account for the stoichiometry. Metal concentrations may be determined by atomic absorption, inductive coupled plasma spectrometric, or another approved method (6, 7). Calibration may be by the method of standard additions or by a calibration curve. If a calibration curve is used, matrix match standards to samples by including 20 mL of 6M HCl per 100 mL for each of the calibration standards. Convert µg/L concentration values to µmoles/L. Multiply the µmoles/L by the solution volume to obtain the µmoles of metal.

14.4 Report the concentrations of each of the metals in the sediment on a µmole per gram dry sediment (µmole/g) basis.

14.5 Calculate the ratio of SEM to AVS:

$$\frac{SEM}{AVS} = \frac{\sum [metal]}{AVS}$$

where SEM is the sum of the concentrations of metals, $\sum [metal]$, for the metals (e.g., cadmium, copper, lead, mercury, nickel and zinc) in Section 14.4 and

AVS is the acid volatile sulfide concentration determined in Section 13.4.

Both SEM and AVS are expressed on a µmole per gram dry sediment (µmol/g) basis. Because metals present in the pore will be included in the analysis, the ratio could be less than that if correction were made for this contribution. This will lead to a conservative estimation of potential bioavailability (1).

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